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BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

POTENTIOMETRIC TITRATIONS

THE USE OF PLATINUM ELECTRODES AND  
CONSTANT READING POTENTIOMETER CIRCUITS

by

John Hall Hopkins  
(Sc.B., Dickinson College, 1932)

submitted in partial fulfillment of the  
requirements for the degree of  
Master of Arts

1934

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UNITED STATES OF AMERICA

DEPARTMENT OF JUSTICE

1957

UNITED STATES OF AMERICA

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THE UNITED STATES OF AMERICA

VS. ALBERT J. BLOOM

JOHN H. HARRIS

(Attorney General, U.S. Dept. of Justice)

and to the United States District Court for the District of Columbia  
for the purpose of obtaining a writ of habeas corpus.

1957



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Electrostatic titrations are of two general types, conductometric and potentiometric. As its name suggests, the basis for the first is the change of electrical conductivity of the solution as the reacting solution is added. In the second type, the titration chamber is made a chemical half-cell by the introduction into the solution of a suitable electrode. By following the voltage change during the titration, the course of the reaction may be followed.

(1) S. S. Taylor, A Treatise on Physical Chemistry, 2nd. ed., S. Van Nostrand Co., New York, 1931, Vol. 2, p. 901.



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POTENTIOMETRIC TITRATIONS  
THE USE OF PLATINUM ELECTRODES AND  
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I. INTRODUCTION.

The use of electrometric titrations is one of the most important of the recent developments in the field of quantitative chemical analysis. The extensive research of the past fifteen years in the use of electrometric methods has given to analytic chemistry a large amount of information of both theoretic and practical interest and importance.

The theoretic basis for electrometric methods of analysis is found in the electrolytic dissociation theory of Arrhenius and the mass action principle, as applied to ionic equilibria. (1)

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The scope of this thesis is limited to a very small part of the potentiometric titration field.

Fundamentally, titrating potentiometrically consists of the determination of the change in voltage characteristic as the reaction is carried out, of the cell formed by the solution and a suitable electrode. There are many methods of forming this cell, depending upon the type of electrodes used. The type of electrode used depends upon the nature of the system. There are, too, many methods of measuring the voltage. The choice of the method of measuring the voltage depends upon the electrodes used and the nature of the system, although the standard potentiometer system is applicable to nearly all electrode systems. Many of the electrode systems are difficult to use and require an expert technician to make and operate. The measurement of the voltage accurately and effeciently, in many methods, requires expensive and extensive equipment. It is the constant objective, therefore, of research to experiment towards simpler methods, more effecient and practical because of less tediousness in manipulation.

The importance and value of this type of analysis can be readily shown by a short survey of its uses and advantages. In general, it can be used for almost any reaction which can be titrated by the usual methods and for all of the most important and well known reactions. The uses of potentiometric titrations are rapidly and constantly increasing in number

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as research brings forth new electrodes and new equipment. This is evidenced by the fact that the literature in this field between 1926 and 1930 is as extensive as for the period between 1892 and 1926. (1)

In research laboratories, whether theoretic, medical or industrial, it is found valuable in all volumetric analysis. By special adaptation, it is found valuable to the medical laboratory in determining hydrogen ion concentration of the body fluids, and to the theoretic laboratory, as a method of interpreting reactions in terms of ionic concentrations and activities.

Its uses in industry are too extensive to attempt a complete list. The following list gives a rough picture of the extent and versatility of its use: acidity in milk, metallic plating solutions, solutions for the treatment of leather, wool scouring liquids, paper sizing, water purification and sewage disposal processes. (2)

The development of constant reading devices has brought a new tool to industry, not only for use in the laboratory but also in the actual processes. The electrodes may be placed in the pipe lines or reaction vessels and the concentrations of the reactants accurately determined and controlled.

In titrating colored or cloudy solutions, where a

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- (2) H. C. Parker, Ind. Eng. Chem., 19, 660 (1927)

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colorimetric indicator change would be difficult to see, or in reactions requiring outside indicators, its advantage over the usual methods is obvious. In the ordinary colorimetric methods it is necessary to make a correction for the difference between the colorimetric end-point and the true equivalence-point. This correction is primarily for the amount of reagent necessary to react with the indicator and to give to the solution color of intensity enough to be detected. In the case of acid-base titration, since few of the ordinary indicators change color at the equivalence-point, another correction is needed. The need for these corrections is eliminated by the use of potentiometric titrations.

The chief disadvantages of this method are the length of time necessary for titration and the extensive amount of equipment used. It is to be noted, however, that with the latest developments, have come the constant reading devices, the use of which makes the time for potentiometric titration as short as for the regular titration, and for some reactions, much shorter. The simplification of equipment, too, has brought into use apparatus which is far less expensive and less difficult to operate.

It is the object of this thesis to study through the scientific literature and, in a more limited manner, in the laboratory some of the latest developments in this field, with a view to determining their adaptability to routine work in

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laboratory. As the title indicates, the use of platinum electrodes and constant reading devices are the problems of major interest. In the field of platinum electrodes, the polarized system and the burette electrode are of special interest. The simpler galvanometer systems as well as electron tube circuits will be studied.

(1) L. M. Kolthoff and E. H. Eyring, *The Determination of Hydrogen Ions*, 2d. ed., John Wiley and Sons, New York, 1933.

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The most fundamental half-cell consists of a metal electrode placed in contact with a solution of its ions. The tendency of the metal to go into solution is called the electrode potential pressure. The opposing pressure is the osmotic pressure of the ions to form molecular form. When an electrode of this type is placed in contact with its solution, a reaction occurs depending upon the difference between the electrode potential pressure and the osmotic pressure of the ions. If the electrode potential is greater the metal goes

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## II. THEORY.

It is advisable at this point to discuss briefly the theory underlying the principle of potentiometric titration. For a complete theoretic explanation of this subject, the reader is referred to "Potentiometric Titrations", by I. M. Kolthoff and N. H. Furman, and the book "The Determination of Hydrogen Ions", by W. M. Clark. (1) (2)

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into solution in the ionic form. This involves leaving upon the electrode a negative charge, an electron. If the osmotic pressure is greater, the metal goes out of solution, involving the gain of an electron from the metal electrode. This reaction will continue until the two electrolytic pressures are equal. The electrolytic solution pressure is constant for the metal electrode but the osmotic pressure of the ion varies with the ionic concentration.

If a method is devised to carry off the electrons from the electrode in the first case or to furnish electrons to the electrode as in the second case, in some continuous manner a current will be drawn from the half-cell and the reaction will be continuous until one of the reactants is gone.

This electrode reaction is represented by:



M represents the metal,  $M^{n+}$  represents the ion.  $n e^-$  gives the number of electrons reacting per ion.

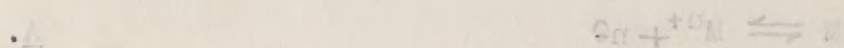
The voltage characteristic of this reaction is represented by:

$$E = - \frac{RT}{nF} \ln \frac{P}{p} \quad \underline{B.}$$

in which R is the gas constant, T the absolute temperature, n the number of electrons reacting per ion, F the charge on one gram equivalent of an ion (one Faraday 96,500 coulombs);  $\ln$  represents the natural logarithm. P is a constant for

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If a cathode is devised to carry off the electrons from the electrode in the first case or to furnish electrons to the electrode as in the second case, in some continuous manner a current will be drawn from the half-cell and the reaction will be continuous until one of the reactants is gone. This electrode reaction is represented by:



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$$E = - \frac{RT}{nF} \ln \frac{P}{Q}$$

in which  $R$  is the gas constant,  $T$  the absolute temperature,  $n$  the number of electrons reacting per ion,  $F$  the charge on one gram equivalent of an ion (one Faraday 96,500 coulombs);  $P$  is a constant for



any given electrode, and represents the electrolytic solution pressure;  $p$  represents the osmotic pressure of the ions and varies with the ionic concentration. This equation is a slight modification of the original Nernst equation.

For practical use this equation is further modified:

$$E = e + \frac{.0591}{n} \log c \quad \text{C.}$$

The constant has been introduced from the relationship between the  $p$  of equation B. and the ionic concentration  $c$  at 25 degrees centigrade, and the change to the decadic logarithms. .0002 is the value for  $R$  divided by  $F$ . The  $e$  represents the constant for the voltage pressure of the  $P$  of equation B.

For complete accuracy the  $c$  should be multiplied by the proper activity coefficient since the theoretic equation holds true only when the activity of the ion is used. However the activity and the concentration are often nearly the same in value. Furthermore, the determination of the activity is still a rather undeveloped field and many of the individual activities are not accurately known. For work in potentiometric titration the use of the concentration gives sufficient accuracy.

There is another mathematical function of concentration which is widely used especially in hydrogen ion work. It is usually signified by a small  $p$  written with the symbol of the ion concerned. Represented mathematically:

$$p_{\text{ION}} = -\log c_{\text{ION}} \quad \text{D.}$$







In order to use this function, equation C. is modified to read:

$$E = e + \frac{.0591}{n} \cdot .0002(t-25) \text{ pION } \underline{E}.$$

There is no method known of measuring the voltage of a single half-cell directly. It is necessary to form a complete cell. This is done by combining the half-cell, to be determined, with another half-cell of known and constant voltage. The internal connection is usually made with a salt bridge. Having now a complete cell, the total voltage may be measured by any one of the many methods available. The voltage of the unknown half-cell is found then from the equation:

$$\text{E.M.F.} = E_{\text{ref}} + E = E_{\text{ref}} + e + \frac{.0591}{n} \cdot .0002(t-25) \text{ pION } \underline{F}.$$

This equation indicates that the voltage measured, E.M.F., is the algebraic sum of the voltages on the two half-cells, written in the order electrode-solution/solution-electrode, according to the accepted conventions concerning the cell. There is a small voltage incurred at the liquid junction but this is so small that it is omitted in potentiometric titration work. This set-up is shown diagrammatically in Figure 1.

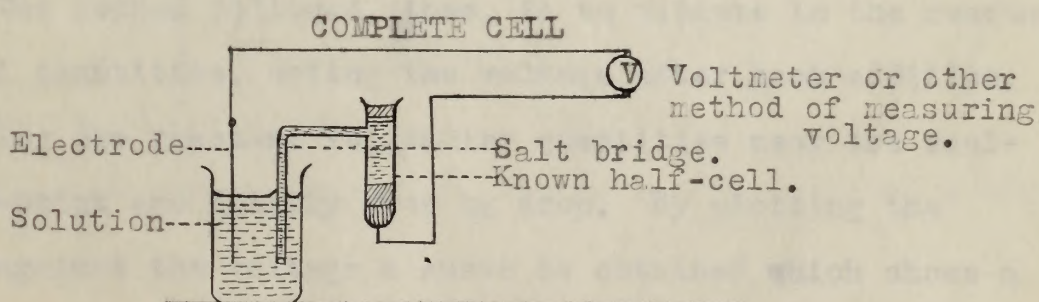


Figure 1.

In order to use this function, equation 2, is modified

to read:

$$E = e + \frac{0.0591}{n} \log \frac{a_{\text{oxid}}}{a_{\text{red}}}$$

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$$E_{\text{cell}} = E_{\text{red}} + e + \frac{0.0591}{n} \log \frac{a_{\text{oxid}}}{a_{\text{red}}}$$

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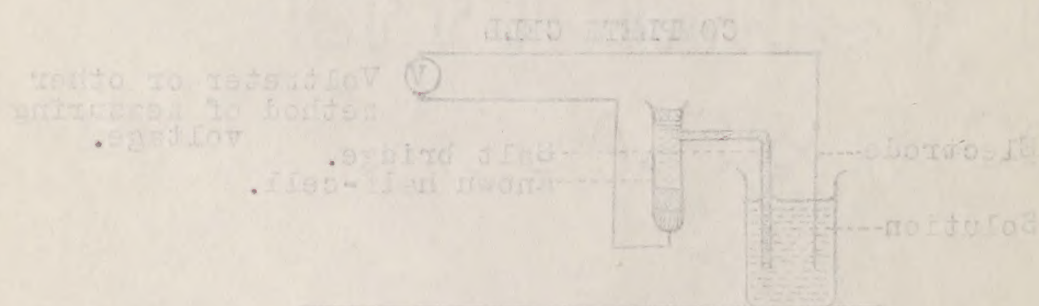


Figure 1.



The methods of measuring the voltage of the cell will be discussed in the next part of this thesis.

It has been shown that the voltage on the electrode in a solution of its ions is a function of the concentration of the ions.

There are three types of reactions used in volumetric analysis: neutralizations, precipitation reactions and oxidation-reduction reactions.

In the neutralization and precipitation reactions, the ion, upon whose concentration the potential depends is changed by the reactant to form a relatively unionized compound. This change in concentration of the ion changes the potential and since this change is greatest near the equivalence-point a break is found in the titration curve.

In oxidation-reduction systems the ratio of the oxidant to the reductant which governs the potential on the indicator electrode. As this ratio changes the potential will change. As the equivalence-point is approached one of the members of the ratio will approach a very small value and the change will be greater causing a break in the titration curve.

The method followed, then, is to titrate in the reactant in small quantities, noting the voltage after each addition, and adding the reactant in smaller quantities near the equivalence-point and finally drop by drop. By plotting the volume against the voltage a curve is obtained which shows a

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decided break at the equivalence-point. This break corresponds to the number of milliliters of reagent equivalent to the amount of the ion present in the sample being titrated. Another method of determining the equivalence-point is to calculate  $\frac{\Delta E}{\Delta c}$  for each addition of the reagent.  $\frac{\Delta E}{\Delta c}$  is the ratio of the potential change with the amount of reagent added. By plotting  $\frac{\Delta E}{\Delta c}$  against the volume of reagent added a curve is obtained which shows a maximum at the equivalence-point. By using  $\frac{\Delta E}{\Delta c}$  the equivalence-point may be determined without the use of a graph, since for the drop at the equivalence-point, this value will be greatest.

Figures 2 and 3 show the titration curves for a typical acid-base titration. The titration equivalence-point is easily detected.

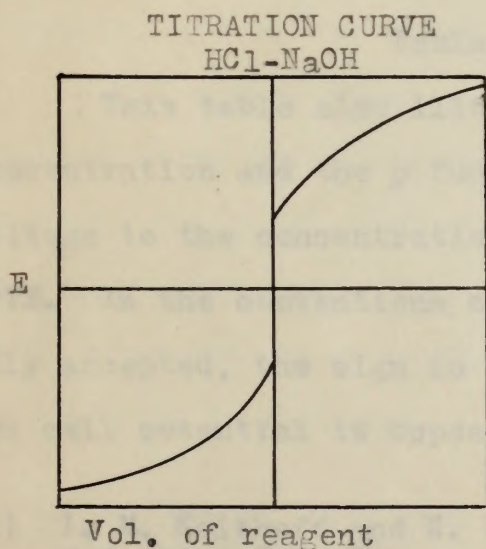


Figure 2. E plotted against volume

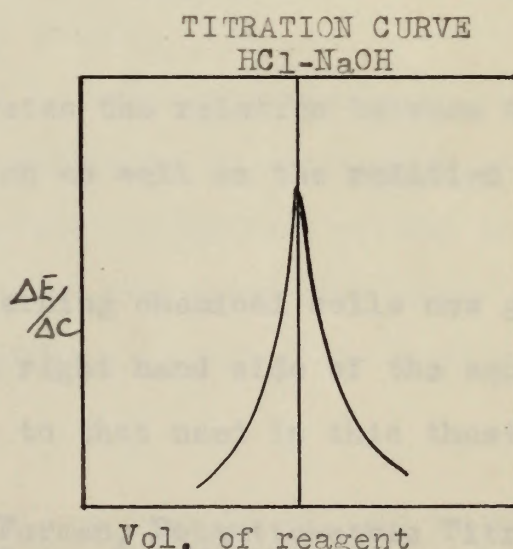
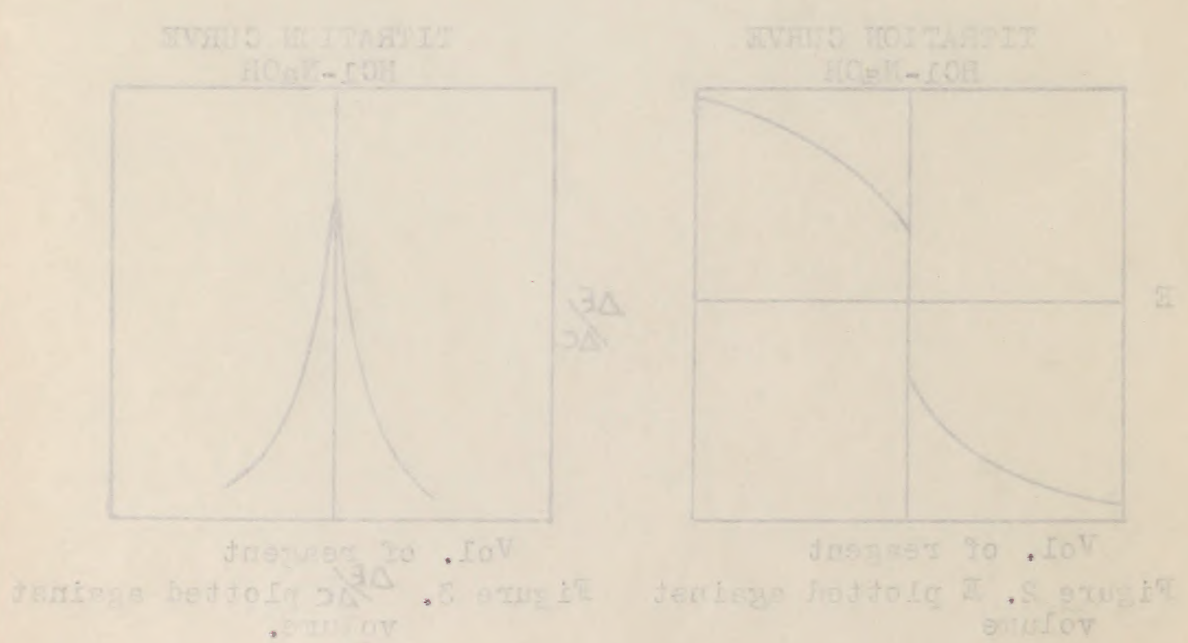


Figure 3.  $\frac{\Delta E}{\Delta c}$  plotted against volume.

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To illustrate even more clearly, Table 1. is presented showing the change in voltage with the concentration and the value  $\Delta E/\Delta c$ . (1)

TITRATION OF HCl WITH NaOH.

Percent neutralized	$[H^+]$	pH	$E_{H_2}$	$\Delta E/\Delta c$
0	$10^{-2}$	2	$e+2 \times .059$	
90	$10^{-3}$	3	$e+3 \times .059$	65
99	$10^{-4}$	4	$e+4 \times .059$	
99.9	$10^{-5}$	5	$e+5 \times .059$	
100	$10^{-7}$	7	$e+7 \times .059$	1180
Excess				
.1	$10^{-9}$	9	$e+9 \times .059$	1180
1	$10^{-10}$	10	$e+10 \times .059$	
10	$10^{-11}$	11	$e+11 \times .059$	65

Table I.

This table also illustrates the relation between the concentration and the p function as well as the relation of voltage to the concentration.

NOTE. In the conventions concerning chemical cells now generally accepted, the sign in the right hand side of the equation for cell potential is opposite to that used in this thesis.

- (1) I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931. p. 29.

To illustrate even more clearly, Table I, is presented showing the change in voltage with the concentration and the

values  $\frac{\Delta E}{\Delta C}$ . (1)

TITRATION OF HCl WITH NaOH.

Percent Neutralized	$[H^+]$	pH	$E_{H_2}$	$\frac{\Delta E}{\Delta C}$
0	$10^{-2}$	2	$+2 \times 10^{-2}$	
20	$10^{-3}$	3	$+3 \times 10^{-2}$	0.5
30	$10^{-4}$	4	$+4 \times 10^{-2}$	
50	$10^{-5}$	5	$+5 \times 10^{-2}$	
100	$10^{-7}$	7	$+7 \times 10^{-2}$	1.50
Excess				
1	$10^{-9}$	9	$+9 \times 10^{-2}$	1.50
10	$10^{-10}$	10	$+10 \times 10^{-2}$	
10	$10^{-11}$	11	$+11 \times 10^{-2}$	0.5

Table I.

This table also illustrates the relation between the concentration and the p function as well as the relation of voltage to the concentration.

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### III. METHODS.

In the preceding section the basic theory of potentiometric titration has been discussed briefly. It is this theory which laid the foundation for the method known as the classical method. The operation of this classical method will be presented followed by a review of the developments in methods in the whole field.

The review is based upon the report and review of progress by N. H. Furman. (1) For complete information, the reader is referred to "Potentiometric Titrations" by I. M. Kolthoff and N. H. Furman, and "The Determination of Hydrogen Ions", by W. M. Clark. (2) (3)

#### The Classical Method.

Figure 4 presents diagrammatically the apparatus and set-up for use in the classical method. (4)

This method makes use of an indicator electrode in a solution to be titrated, and a reference electrode, of constant and known potential. By titrating in portions of the reactant and determining the voltage between the electrodes after each addition as explained in the foregoing section the course of the reaction is followed.

- (1) N. H. Furman, Ind. Eng. Chem., Analyt. Ed., 2, 213 (1930).
- (2) I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931.
- (3) W. M. Clark, The Determination of Hydrogen Ions, 3rd. ed., Williams and Wilkins Co., Baltimore, Md., 1928.
- (4) I. M. Kolthoff and N. H. Furman, op. cit., p. 94.

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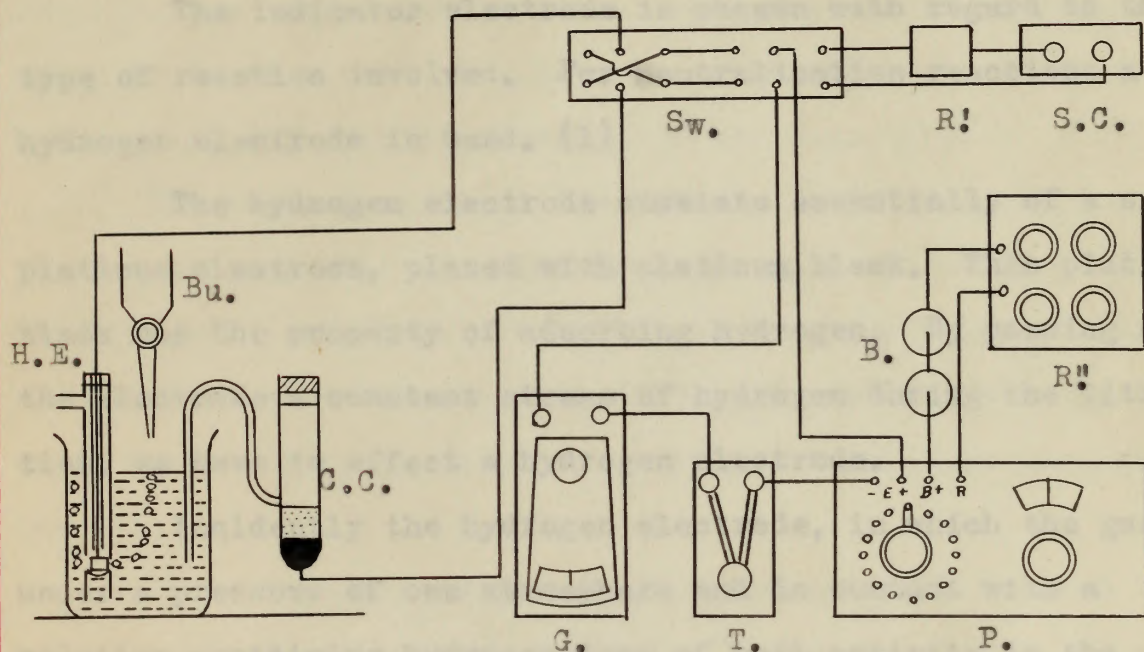
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- (1) H. H. Burman, Ind. Eng. Chem., Analyt. Ed., 2, 212 (1930).
- (2) I. M. Kolthoff and H. H. Burman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931.
- (3) W. M. Clark, The Determination of Hydrogen Ions, 3rd. ed., Williams and Williams Co., Baltimore, Md., 1928.
- (4) I. M. Kolthoff and H. H. Burman, op. cit., p. 64.



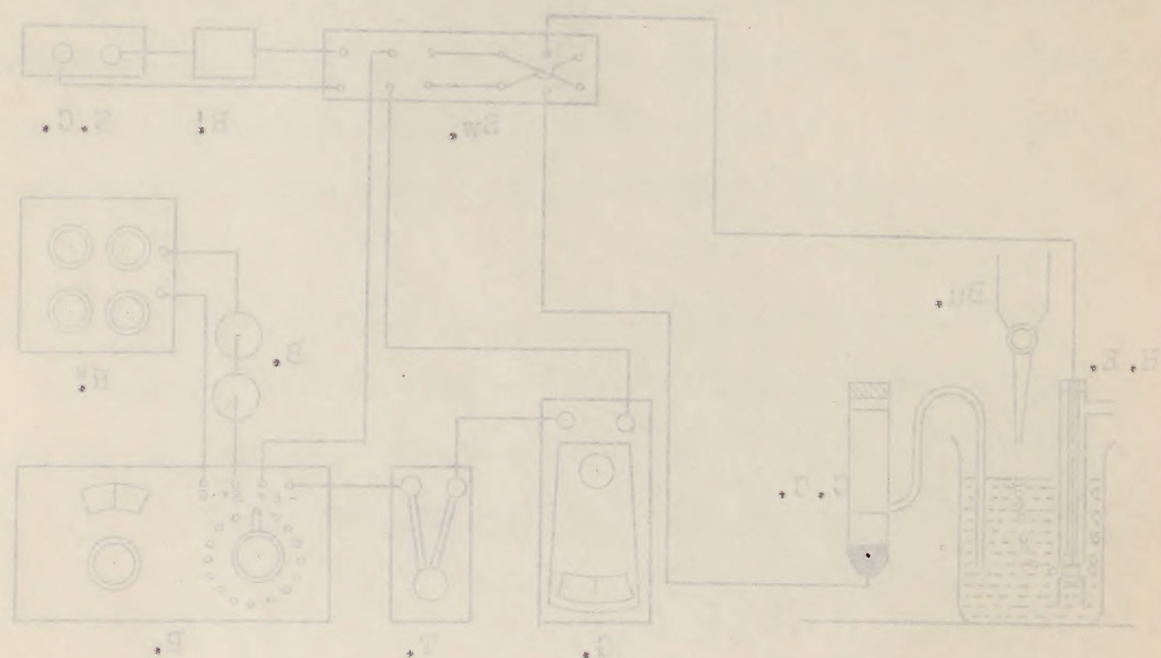
# CLASSICAL METHOD OF POTENTIOMETRIC TITRATION



- S.C. Standard cell.
- R! High resistance to protect S.C.
- Sw. Switches.
- R! Variable resistance.
- B. Dry cells.
- P. Student potentiometer
- T. Tapping key.
- G. Galvanometer.
- C.C. Calomel cell or other reference electrode.
- Bu. Burette.
- H.E. Hydrogen electrode or other indicator electrode.

Figure 4.

## CLASSICAL METHOD OF POTENTIOMETRIC TITRATION



S.C. Standard cell.  
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Figure 4.



The equivalence-point is determined by one of the methods mentioned.

The indicator electrode is chosen with regard to the type of reaction involved. For neutralization reactions a hydrogen electrode is used. (1)

The hydrogen electrode consists essentially of a small platinum electrode, plated with platinum black. This platinum black has the property of adsorbing hydrogen. By passing over the electrode a constant stream of hydrogen during the titration, we have in effect a hydrogen electrode.

Incidentally the hydrogen electrode, in which the gas is under a pressure of one atmosphere and in contact with a solution containing hydrogen ions of unit activity is the standard for the electrode potential for all electrodes.

The use of the hydrogen electrode is a simple example of the fundamental theory of the cell. The potential on the electrode varies with the concentration of the hydrogen ion. Table 1 and Figures 2 and 3 show the result typical of this type of titration.

In an oxidation-reduction reaction, the indicator electrode usually used is a small platinum electrode. (2) The most successful type is a small bright platinum wire. This electrode has been found capable of following an oxidation-reduction reaction.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 200.  
Cf. Determination of Hydrogen Ions, Clark, p. 221.

(2) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 45, 254.

- (1) Cf. Potentiometric Titrations, Kolthoff-Irwin, p. 200.
- (2) Cf. Determination of Hydrogen Ions, Clark, p. 291.
- (3) Cf. Potentiometric Titrations, Kolthoff-Irwin, p. 45, 254.

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The precipitation of the silver ion from a solution by the use of a soluble chloride is an example of the type of precipitation reaction. In this case a silver electrode is used to follow the decrease in silver ion concentration. It might be noted that a chlorine electrode might also be used in this titration.

For a reference electrode a half-cell must be used that has a constant and known potential. There are several of these in use. The two most used are the calomel cell and the silver chloride half-cell.

The calomel cell is for most purposes the most practical. It has all of the characteristics essential to the successful half-cell. Its potential is little changed by change in temperature and this change has been accurately measured. It is fairly simple to construct and, when made carefully, gives the theoretic potential reproducibly. Barring contamination, it is stable. (2)

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- (1) Cf. Potentiometric Titrations, Kolthoff-Furman, p.9.
- (2) Cf. The Determination of Hydrogen Ions, Clark, p. 303.

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contact with its salt mercurous chloride, in the presence of a solution of potassium chloride. The potential of the cell varies with the concentration of the potassium chloride solution. It is, therefore, of great importance that the solution of potassium chloride be accurately known concentration. There are three concentrations of potassium chloride which are in general use and for which most of the measurements have been made. They are .1 normal, saturated and the standard, the normal solution. Contact is made with the outside circuit by means of a platinum wire dipping into the mercury but not in contact with any of the other constituents of the cell. The contact with the other half-cell is made by means of a salt bridge usually containing a saturated solution of potassium chloride. If the solution to be titrated contains silver or mercury ions, the salt bridge should be filled with the nitrate or sulphate.

The silver chloride half-cell consists of a silver wire, the surface of which has been coated by electrolytic methods with silver chloride. The silver wire leads to the outside circuit. A solution of potassium chloride surrounds the wire and forms a salt bridge to the solution. This cell has the disadvantage of being light sensitive, so must be used in the dark or mounted in a light proof container. It is difficult to make this cell accurately. In other words the potential is not reproducible. (1)

(1) A. A. Noyes and J. H. Ellis, J. Am. Chem. Soc., 39, 2532 (1917)

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(1) A. A. Weiss and J. H. Miller, J. Am. Chem. Soc., 52, 2522 (1930)



It is readily seen that a method of measuring voltage must be used which does not draw current of an appreciable amount from the cell. Although a voltmeter would be the simplest method of measuring the voltage, unless this were in series with a high resistance, current would be drawn from the cell to an amount great enough to cause considerable error. The standard method of measuring the voltage is to make use of the potentiometer system. (1) A simple form of the potentiometer system is shown diagrammatically in Figure 5.

#### SIMPLE POTENTIOMETER SYSTEM

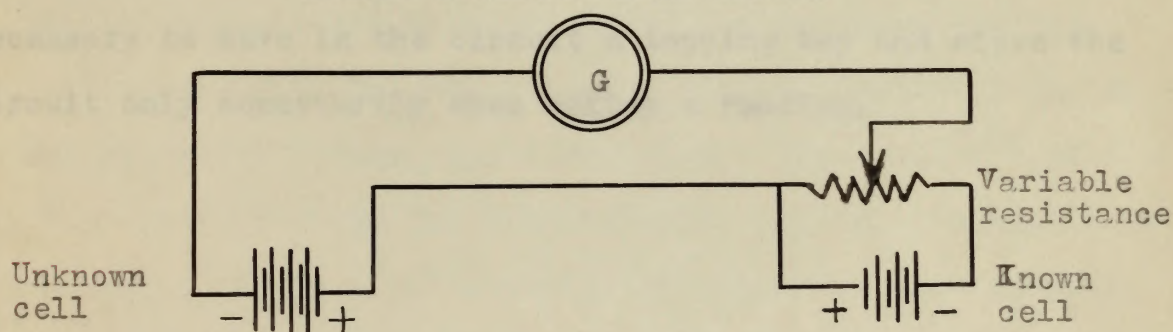


Figure 5.

In a few words, the theory of this electrical circuit is to oppose the voltage to be measured with an equal voltage. When this condition exists a galvanometer in the system will read zero showing that no current is passing. The opposing potential is varied with a resistance. By measurement of the resistance necessary to balance the unknown potential, the unknown potential may be determined. For this purpose the resistance is usually calibrated and used with a known cell.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 84.

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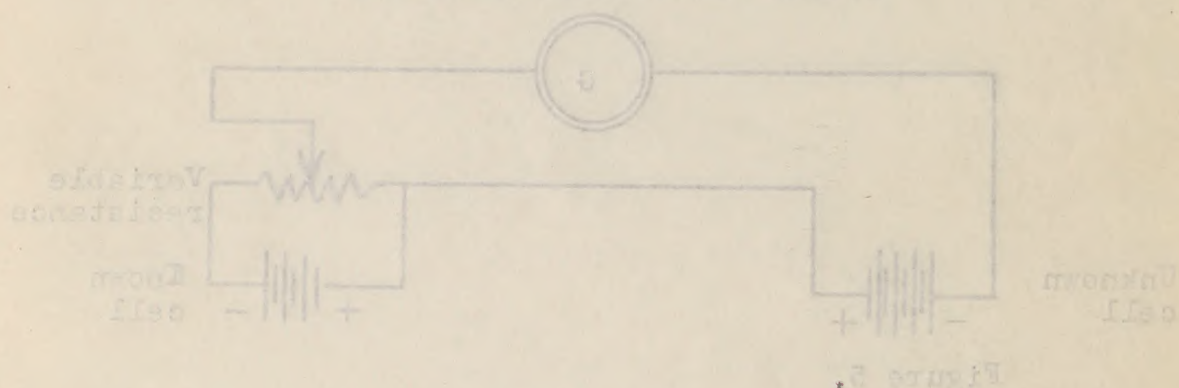


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(1) Cf. Potentiometric Titrations, Kolthoff-Irwin, p. 64.



The potentiometer apparatus used in potentiometric titrations is included in Figure 4. In this apparatus a specially calibrated resistance or potentiometer is used, so that when the potentials balance the potentiometer reads the voltage directly. The source of opposing current is from dry cells, which have been calibrated against a standard cell such as the Weston cell. This calibration is necessary at the beginning and end of each titration. The potentiometer system minimizes the amount of current taken from the solution, but it is necessary to have in the circuit a tapping key and close the circuit only momentarily when making a reading.

A large potential between the electrodes. This method involves the necessity of using the potentiometer system. A null point instrument, such as a galvanometer or milliammeter, is all of the measuring apparatus necessary.

Pitts<sup>1</sup> and Freedwell<sup>2</sup> developed this system in about the same time but independently. By using a galvanometer as a sensitive voltmeter in series with a high resistance, Freedwell was able to make this system function readily.

While this system is very simple in operation and cost, it has the decided disadvantage of necessitating a different electrode system for each titration. The difficulty in determining the effect of foreign electrolytes in the solution and for the effect of temperature makes for inaccuracies.

- (1) E. R. Farnham, *Ind. Eng. Chem., Anal. Ed.*, 2, 422, (1930).
- (2) G. C. Potentiometric Titrations, Freedwell-Kellogg, p. 28.

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There are four other fundamental methods of potentiometric titration: titration to zero difference in potential; polarized indicator electrodes; electrode system consisting of two metallic electrodes; and differential titration. Each is a special modification of the classical method. (1)

#### Titration to Zero Difference in Potential. (2)

This system is constructed by substituting for the standard calomel cell a reference electrode of potential identical to that of the titration solution and its electrode at the equivalence-point. The equivalence-point is marked, then, by a zero potential between the electrodes. This method obviates the necessity of using the potentiometer system. A null point instrument, such as a galvanometer or capillary electrometer, is all of the measuring apparatus necessary.

Pinkhof and Treadwell developed this system at about the same time but independently. By using a galvanometer or simple but sensitive voltmeter in series with a high resistance, Treadwell was able to make this system constant reading.

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- (1) N. H. Furman, Ind. Eng. Chem., Analyt. Ed., 2, 213, (1930)  
(2) Cf. Potentiometric Titrations, Furman-Kolthoff, p. 95.



There are four other fundamental methods of potentiometric titration: titration to zero difference in potential; titration to a constant potential; titration to a constant current; and differential titration. Each is a special modification of the classical method. (1)

Titration to Zero Difference in Potential. (2)

This system is characterized by substituting for the standard and calomel cell a reference electrode of potential identical to that of the titration solution and the electrode of the equivalence-point. The equivalence-point is then, by a zero potential between the electrodes. This method obviates the necessity of using the potentiometer system. A null point instrument, such as a galvanometer or capillary electrometer, is all of the measuring apparatus necessary.

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(1) M. H. Pittet, *Ind. Eng. Chem., Anal. Ed.*, 2, 215, (1930)  
 (2) G. Treadwell, *Potentiometric Titrations*, Butterworths, p. 65.



results.

Mlle. Bouchere has modified this system slightly, for use in metallic ion determination. Using two identical electrodes, one in the unknown solution and the other in a known solution, she forms a complete cell. The solution of known concentration is more dilute than that of the unknown concentration. By titrating into the unknown solution pure water, the concentration of the two may be made identical. At this point the voltage between the two will be zero. The disadvantages of the original system are inherent to this system.

Müller measures the potential of the equivalence-point and uses this value to oppose the potential of the titration cell. This is another modification of the null-point method. The difficulty of making the potential equivalence-point measurements, makes this system unsatisfactory. There are, too, other influences which make the equivalence-point potential vary even in consecutive titrations.

#### Polarized Indicator Electrodes.(1)

It is inadvisable in some cases to use a metal corresponding to the ion in solution as an electrode. Dutoit and vonWeisse devised the polarized electrode for the purpose of replacing this electrode. A platinum electrode is polarized cathodically by means of a small polarizing electrode carrying a small **current**. The platinum indicator electrode is kept

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.

results.

Miss Bronner has modified this system slightly, for use in catalytic determination. Using two identical electrodes, one in the unknown solution and the other in a known solution, she forms a complete cell. The solution of known concentration is more dilute than that of the unknown concentration. By titrating into the unknown solution pure water, the concentration of the two may be made identical. At this point the voltage between the two will be zero. The disadvantages of the original system are inherent to this system.

Miller measures the potential of the equivalence-point and uses this value to oppose the potential of the titration cell. This is another modification of the null-point method. The difficulty of seeking the potential equivalence-point measurements, makes this system unsatisfactory. There are, too, other influences which make the equivalence-point potential very easy to come into titrations.

# Polarized Indicator Electrodes (1)

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(1) Cf. Potentiometric Titrations, Kolthoff-Watson, p. 104.



plated with a light layer of the metal giving it the characteristic potential of the metal in question. This system, while applicable to a few titrations, is essentially inaccurate due to the loss in metal by the plating from the solution.

#### Electrode System Consisting of Two Metallic Electrodes.(1)

In this system, both the indicator electrode and the reference electrode are replaced by metallic electrodes, both of which are in the unknown solution. In one variation of this method two platinum electrodes are used given different potentials by means of a low polarizing current. In the other the two electrodes are of dissimilar metals, which have been found capable of following the reaction to be studied. Both systems are essentially the same in theory.

The simplicity of this system in the preparation of the electrodes is an advantage. The danger of diffusion error, characteristic to the use of any type of salt bridge is eliminated. The ease with which this system can be used when an inert atmosphere is necessary for the titration is another important advantage. It is not possible to measure oxidation-reduction potentials directly or pH values with this system. In fact the potentials may vary from titration to titration, due to the effect of the preparation of the electrode. It is

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.



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found, however, to be an accurate method of titration, since it is not the absolute potential, which is in this case important but the relative values in the one titration. It should be noted that some metallic electrodes have been found which can be used for pH values and similar work, but in general this system is not applicable to such work.

Much of the recent research has been done in this field. Its practical advantages and the high degree of accuracy with which the titration may be made by this system make it of fundamental importance.

Since this field is the major subject of this thesis, it will be presented thoroughly in the next section.

#### Differential Titration. (1)

This system is another which is characterized by a high degree of accuracy. In ease of use, however, it is second to the bi-metallic system, since in most differential titration methods, special apparatus is used which requires experience to operate.

In this system two metallic electrodes are used, usually of the same metal and often platinum. One of the electrodes is in contact with the main body of the solution and the other is placed in a small portion of the solution isolated mechanically from the main body of the solution. This causes a difference in potential between the electrodes which is at a

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 112.

found, however, to be an accurate method of titration, since it is not the absolute potential, which in this case is important but the relative values in the one titration. It should be noted that some metallic electrodes have been found which can be used for redox and similar work, but in general this system is not applicable to such work.

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(1) Cf. Potentiometric Titrations, Kolthoff-Irman, p. 112.



maximum at the equivalence-point. The titration curve of this system resembles that of the  $\frac{\Delta E}{\Delta c}$  curve of the classical method.

D. C. Cox seems to have been the first to introduce this method. His method involves the titration of aliquot portions of the unknown solution simultaneously. The solutions are contained in separate beakers and connected by means of a salt bridge. The reacting solution is run in by means of two burettes. The total amount run into the first is kept at a constant amount greater than that run into the second by about .1 to .2 milliliters. The electrodes used are two platinum electrodes, one in each solution. The potential between these two electrodes will be different and have a maximum difference when the first has reached the equivalence-point.

This system has many advantages. It is very accurate. It eliminates the necessity of plotting curves. Diffusion troubles incident to the use of the salt bridge are eliminated since both solutions so connected are of nearly the same concentration.

MacInnes and his co-workers have done much work in modifying the work of Cox. In general their system is to have both electrodes in the one container. A small portion of the solution is isolated from the rest of the solution mechanically and is in contact with one of the electrodes. After the addition of a portion of the reagent, there is a difference of potential between the electrodes due to the fact that they

examine at the sensitive point. The first in order of this system consists of the ~~the~~ sensitive method.

D. G. Cox would have been the first to introduce this method. This method involves the use of a solution of the unknown solution electrolytically. The solutions are contained in separate vessels and connected by means of a bridge. The resulting solution is run in by means of two bottles. The total amount run into the second by about constant amount greater than that run into the second by about

1. to 2 milliliters. The electrodes used are two platinum electrodes, one in each solution. The potential between these two electrodes will be different and have a maximum difference when the first has reached the sensitive point.

This system has many advantages. It is very accurate. It eliminates the necessity of standard curves. Distortion troubles incident to the use of the salt bridge are eliminated since both solutions are connected and of nearly the same concentration.

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are in solutions of different concentration. After making the reading of the voltage, the isolated portion of the solution is mixed with the rest before another addition of the reagent is added. This procedure is carried up to the equivalence-point, at which point the electrodes will have the greatest difference in potential.

These modifications eliminate the use of two burettes, are simpler to operate, yet just as accurate.

The latest apparatus by MacInnes and Dole (1) is worthy of note for its simplicity and for its ingenious apparatus. It is shown diagrammatically in Figure 6. The glass shield isolates part of the solution surrounding the one electrode. The isolated portion of the solution is mixed with the rest, when necessary by means of a gas lift pump. The burette stopcock is so constructed that it regulates the supply of gas to the lift pump as well as admitting the reagent. When the reactant is being added to the main portion of the solution, no gas can flow. By turning the stopcock one-eighth turn, the reagent is cut off as well as the gas. The reading is now made. By completing a quarter turn from open, the gas is allowed to flow mixing the isolated portion with the rest of the solution.

The burette electrode (2) is usually included in this field although its titration curve is not similar to those of

- (1) D. A. MacInnes and M. Dole, J. Am. Chem. Soc., 51, 1119(1929)  
(2) H. Willard and A. W. Boldyreff, J. Am. Chem. Soc., 51, 471(1929)



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solution.

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cell although the titration curve is not similar to those of

- (1) D. A. Kellner and W. Dole, J. Am. Chem. Soc., 51, 1113 (1929)
- (2) R. Willard and A. E. Goldberg, J. Am. Chem. Soc., 51, 1711 (1929)



the regular differential titration. It is shown in Figure 7. It is simple in construction, yet accurate in results. A small platinum wire is sealed into the tip of the burette below the stopcock. This forms a half-cell with the reagent solution and thereby serves as a reference electrode. The indicator electrode is usually a platinum wire. The tip of the burette is placed under the surface of the solution to be titrated and acts as a salt bridge. It has been found experimentally that there is no appreciable diffusion error. This may be accounted for by the fact that the reagent is flowing into the solution most of the time during the titration.

DIFFERENTIAL TITRATION  
APPARATUS

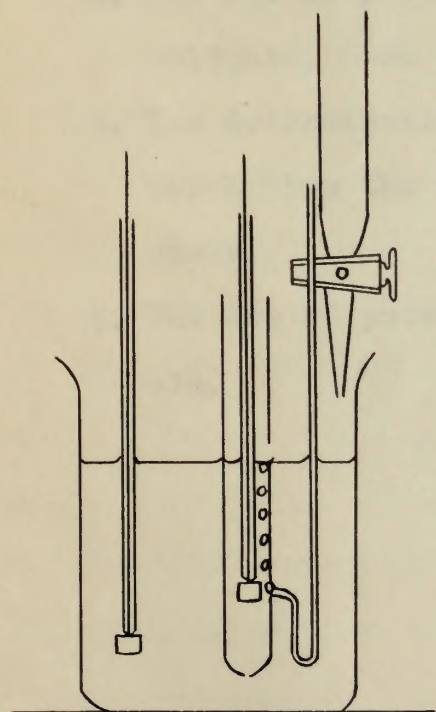


Figure 6. Apparatus of  
MacInnes and Dole.

THE BURETTE  
ELECTRODE

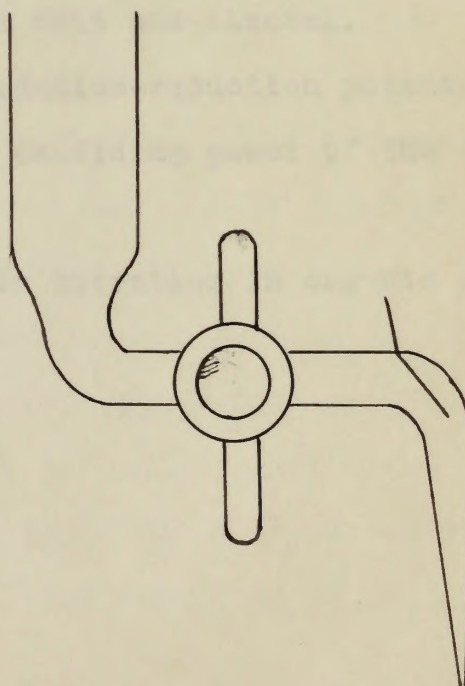


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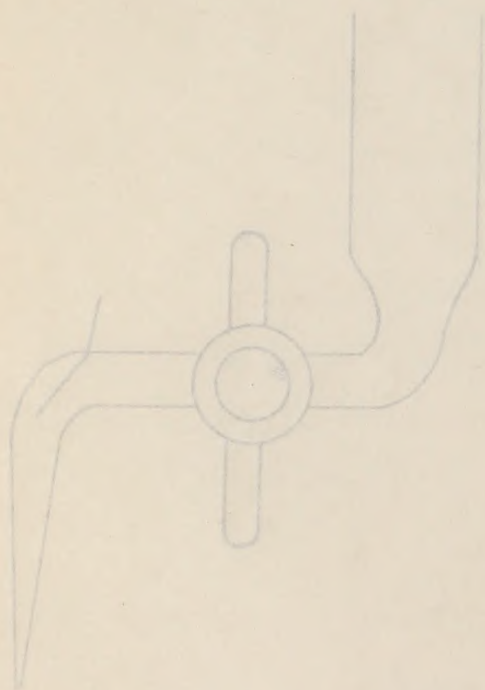


Figure 7.

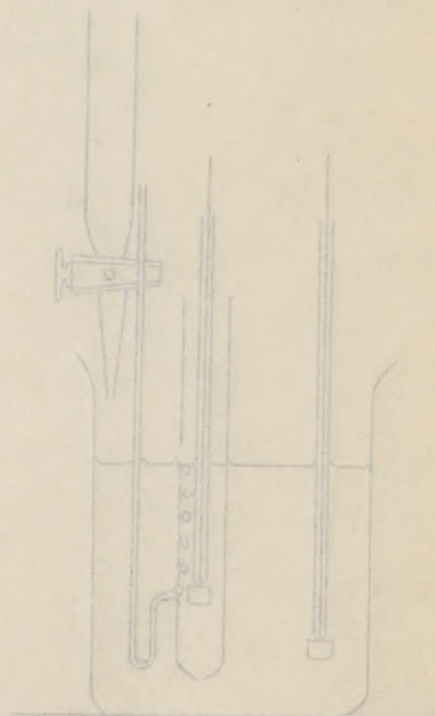


Figure 8. Apparatus of  
MacInnes and Dole.



Since the interest of this thesis is one of method, a resume of most of the important methods has been given before the discussion of the one system chosen for study.

It is of interest also, to list other fields of research in potentiometric titrations and its special modifications. (1)

1. Determination of pH at which quantitative reactions take place most effeciently. (Not necessarily volumetric)
2. Potentiometric micro-titration.
3. Development of new electrodes, especially for use in neutralization reactions.
4. The use of potentiometric titrations in non-aqueous solvents, such as acetic acid and alcohol.
5. The determination of oxidation-reduction potentials, which show the relative oxidizing power of the reagents.
6. The use of potentiometric titration in organic analysis.

(1) N. H. Furman, Ind. Eng. Chem. Analyt. Ed., 2, 213, (1930)

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sis.



#### IV. BIMETALLIC ELECTRODE SYSTEMS.

This system of potentiometric titration was mentioned in the last section. The simplicity of this system was pointed out, as well as the various advantages connected with its use.

Hostetter and Roberts, while investigating the use of a palladium electrode as an indicator electrode in an oxidation-reduction reaction, found that the voltage between it and a half-cell remained almost constant throughout the titration and no break was observed at the equivalence-point. (1)

F. Müller has shown that this behavior is true only of such reactions in hydrochloric acid solutions and is due to surface change in the metal. (2)

The discovery of this unique action of palladium, however, suggested a complete study of the metallic electrode systems for use in potentiometric titrations.

Willard and Fenwick and later VanName and Fenwick made extensive investigation in this field and much of the basic work was contributed by their research.

Willard and Fenwick first took up the problem in 1920. They first verified the work of Hostetter and Roberts. (3) A strip of palladium was used for a reference electrode and a platinum wire for an indicator electrode. A sharp but transient equivalence-point was found. The transient nature of

- (1) J.C.Hostetter and H.S.Roberts, J.Am.Chem.Soc., 41, 1337(1919)
- (2) F.Müller, Z. Elektrochem., 34, 237 (1928)
- (3) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 44, 2504 (1922)

#### IV. EXPERIMENTAL METHODS

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- (1) E. J. Hostetler and E. S. Roberts, J. Am. Chem. Soc., 41, 1337 (1919)
- (2) E. Miller, Z. Elektrochem., 34, 237 (1930)
- (3) E. R. Willard and E. Tannick, J. Am. Chem. Soc., 44, 1901 (1922)



the break with the palladium made its use as a reference electrode unsatisfactory. In further investigation they found that even the first break came after the equivalence-point, causing considerable error. By reducing the surface of the palladium, the error was lessened but the operation was still unsatisfactory. It was found that this property of palladium is characteristic of oxidation-reduction reactions in which a quantity of strong hydrochloric acid is present. In dilute hydrochloric acid solutions or in sulfuric acid, no break was found in a titration curve. The conclusion was made that the palladium was attacked, which caused the presence of another reducing agent besides the one being titrated.

An alloy of gold and palladium was tried, but the results obtained were irregular and too high. A platinum-palladium alloy electrode was then used. In this case, too, evidence of attack on the palladium was apparent.

The best results were obtained with a small wire of platinum-palladium in place of the foil previously used. It was found that even this showed signs of attack after several titrations.

The work with palladium suggested that other metals might give better results and extensive investigation was started.

In the work with palladium all reactions studied consisted of various solutions of dichromate and ferrous iron. In

the work with the galvanometer was its use as a reference electrode and as a cell. In further investigation they found that even the first series of cells the equilibrium-point, changing considerably. By reducing the surface of the electrode, the error was lessened but the equilibrium was still unsteady. It was found that this property of palladium is characteristic of oxidized or reduced reaction reactions in which a quantity of strong hydrochloric acid is present. In dilute hydrochloric acid solutions or in sulfuric acid, no break was found in a titration curve. The conclusion was made that the palladium was attacked, which caused the presence of another reducing agent besides the one being titrated.

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The best results were obtained with a small wire of platinum-palladium in place of the cell previously used. It was found that even this showed signs of attack after several minutes.

The next step was to use other metals in place of the palladium and extensive investigation was made.

In the work with the galvanometer, various metals were used of various amounts of thickness and various sizes. In



the following work the use of permanganate and other oxidants and reductants was also studied.

The system of a platinum indicator electrode and a platinum-rhodium alloy reference electrode was found to give good results. The accuracy was found to depend upon the acidity. In the reaction involving dichromate, solutions containing less than 50% of hydrochloric acid were found to give excellent results, and when sulfuric acid was used 20% seemed optimum. The results in the use of permanganate were slightly irregular.

Because of the resistance to acid action of tungsten, this metal seemed to offer a promising electrode material. Accurate breaks were obtained using the tungsten against both platinum and the regular half-cell and also against the platinum-rhodium alloy electrode. The results were better in the case of the dichromate than with the permanganate. By the addition of manganous sulfate to the solution, it was found that the permanganate could be used with this electrode accurately even in the presence of hydrochloric acid. In all titrations the magnitude of the equivalence-point break was small.

The research was continued using other metals of the unattackable class. Molybdenum, tantalum, iridium, osmium and gold, in combinations of each other, with palladium, with tungsten, with platinum, with platinum-rhodium were all experimented with. The use of platinum alloys of these metals and

the following: (a) the use of germanium and other elements and a discussion of the results.

The study of a silicon-germanium alloy was made and a silicon-germanium alloy reference electrode was found to give a constant potential. The electrode was found to be stable in the solution. In the reaction involving hydrogen, silicon and germanium, the reaction of hydrogen with silicon was found to give a constant potential, and then silicon was used as a reference electrode. The results of the use of germanium were also irregular.

Because of the resistance to self-action of tungsten, this metal was used as a standard electrode material. Accurate results were obtained using the tungsten against both platinum and the silver-silver chloride and also against the hydrogen-silver-silver chloride. The results were better in the case of the silver-silver chloride than the hydrogen-silver-silver chloride. By the addition of hydrogen chloride to the solution, it was found that the hydrogen-silver-silver chloride electrode accurately, even in the presence of hydrochloric acid. In all directions the magnitude of the equilibrium-point break was small.

The research was continued using other metals of the transition series. Molybdenum, vanadium, niobium, tantalum and zirconium, in combinations of each other, with platinum, with tungsten, with silver-silver chloride were all examined with. The use of platinum alloys of these metals and



other alloys of these metals were tried.

Briefly the investigation showed the following combinations to be the most satisfactory: Pt, Pt-Rh; W, Pt; W, Pt-Rh. All palladium electrodes whether pure or alloys were found to be unsatisfactory.

The character of the bimetallic system is different from that of the ordinary metallic, half-cell system.

Figure 8 shows a characteristic titration curve. It will be noted that the potential read does not vary from a small quantity until very close to the equivalence-point. The equivalence-point is marked by a sharp rise. Tungsten is an exception. Its curve shows a gradual rise during the titration with the characteristic sharp rise at the equivalence-point.

The magnitude of the potential difference at the equivalence-point is less in the bimetallic system than in that involving a half-cell. The magnitude of the bimetallic system break will vary from titration to titration, although it always occurs at the equivalence-point. The magnitude of the break also varies with the method of pre-treatment.

An excess of the oxidizing reagent brings various results. In any combination with platinum, in a solution in which dichromate is used, the potential after the equivalence-point break may rise slightly, fall slightly or remain constant depending upon the amount of acid present. In the reactions involving permanganate a very sharp decrease in potential is found in an excess of the oxidant. In systems



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involving tungsten only a slight "crawl" usually to a higher potential is found in an excess of the oxidant.

It was found that the magnitude of the break was greater and sharper when sulfuric acid was used than when hydrochloric acid formed the acid medium.

In order to study the equivalence-point phenomenon, a half-cell was also placed in the solution and the system arranged so that throughout the titration the potential on both metallic electrodes could be determined.

Figure 9 shows typical curves resulting from such an experiment. It illustrates clearly the function of the two electrodes.

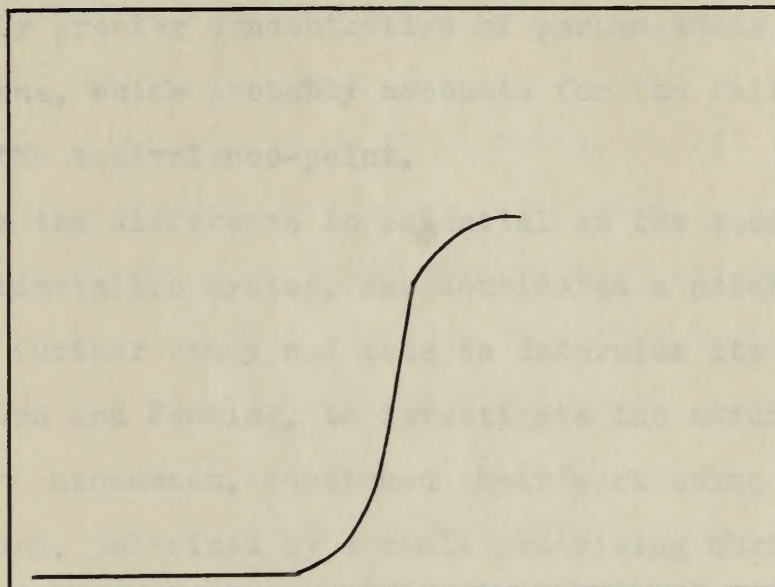
Initially in the presence of the reducing agent alone, the potential of the two electrodes is different. On the addition of a slight amount of oxidizing agent this difference falls to zero, and remains at that value to within a half a milliliter of the equivalence-point. As the equivalence-point is approached the electrodes begin to function differently, having a maximum difference at the equivalence-point. While this difference always exists at the equivalence-point, its magnitude varies. The individual electrode potential differs too, depending upon their pre-treatment and may change after use. Platinum is normally positive to its alloys and to tungsten. Its polarity may change with its alloys after use. Between platinum and tungsten, however, there is never a reversal of polarity although the difference does vary.





# EQUIVALENCE-POINT BREAK WITH BIMETALLIC ELECTRODES

E.M.F.

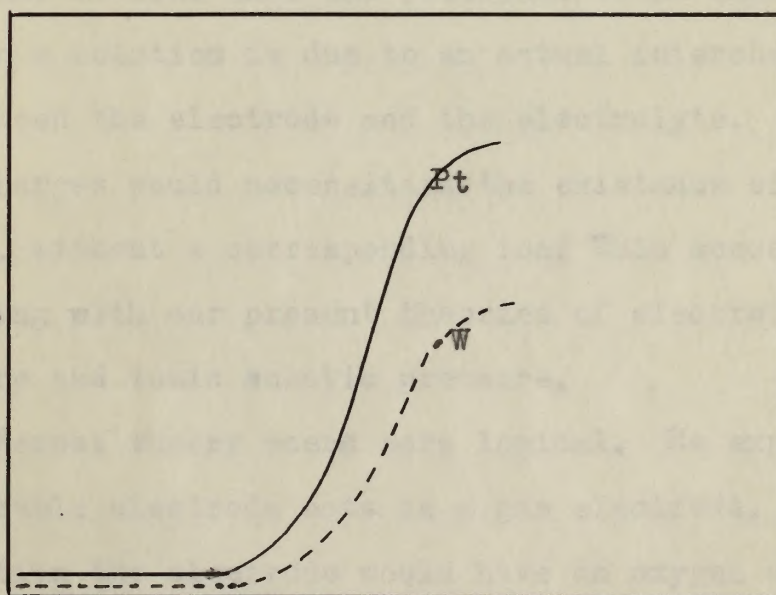


Volume of reagent.

Figure 8.

## POTENTIAL ON THE TWO METALLIC ELECTRODES

E.M.F.



Volume of reagent

Figure 9.

# EQUIVALENT-POINT BREAK WITH BIMETALLIC ELECTRODES

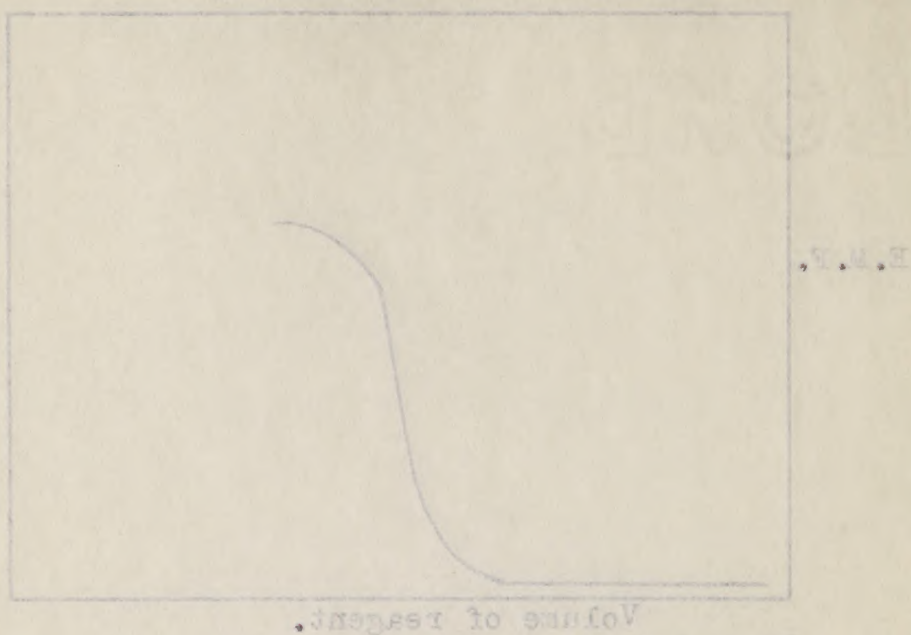


Figure 8.

## POTENTIAL ON THE TWO METALLIC ELECTRODES

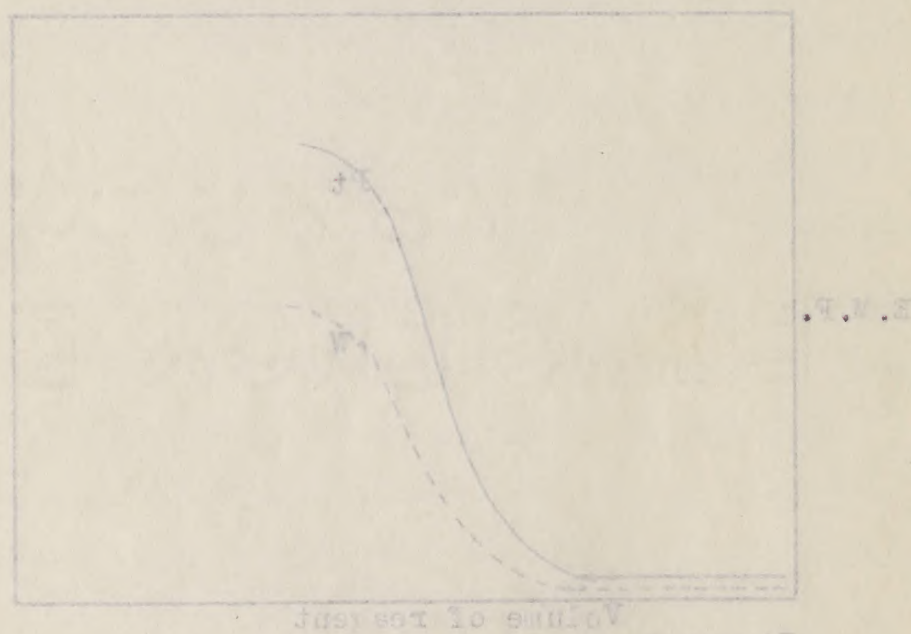


Figure 9.



The break in the platinum-rhodium alloy electrode occurs in a slightly greater concentration of permanganate than with platinum alone, which probably accounts for the fall in potential after the equivalence-point.

Since the difference in potential at the equivalence-point of a bimetallic system, was considered a polarization phenomenon, further study was made to determine its nature.

Willard and Fenwick, to investigate the nature of this polarization phenomenon, continued their work using two platinum electrodes, polarized by a small polarizing current. (1)

As to why two unattackable electrodes standing side by side in the same solution should have a different potential, there are two basic theories.

LeBlanc reasons that the potential on an unattackable electrode in a solution is due to an actual interchange of charges between the electrode and the electrolyte. This exchange of charges would necessitate the existence of a charge, an electron, without a corresponding ion. This conception is not in keeping with our present theories of electrolytic solution pressure and ionic osmotic pressure.

The Nernst theory seems more logical. He explained that the unattackable electrode acts as a gas electrode. In an oxidizing solution the electrode would have an oxygen charge and in a reducing solution a hydrogen charge.

(1) H.H. Willard and R. Fenwick, J. Am. Chem. Soc., 44, 2516 (1922)



33  
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Since the difference in potential of the equivalence-point of a titration system, was considered a constant phenomenon, further study was made to better the nature of this. Willard and Denwick, to investigate the nature of this polarization phenomenon, continued their work using two platinum electrodes, polarized by a small polarizing current. (1)

As to why the unattachable electrodes at either side of the solution should have a different potential, there are two theories.

Lehmann reasons that the potential on an unattachable electrode in a solution is due to an actual interference of charges between the electrode and the electrolyte. This exchange of charges would necessitate the existence of a charge on the electrode, without a corresponding ion. This conception is not in keeping with our present theories of electrolytic solution pressure and ionic osmotic pressure.

The Helmholtz theory seems more logical. He explained that the unattachable electrode acts as a gas electrode. In an oxidizing solution the electrode would have a net negative charge and in a reducing solution a hydrogen charge.

(1) H.H. Willard and F. Denwick, J.A. Chem. Soc., 55, 2216 (1933)



The Nernst theory was further developed by Fredenhagen.<sup>(1)</sup> Willard and Fenwick explained their bimetallic electrode system on the basis of this theory.

The theory is based on the hypothesis that an unattackable electrode may form a solution with a gas. It is known that gases do dissolve in platinum and other metals. It is also to be noted that in a vigorous reduction hydrogen is actually liberated in amounts great enough to be readily identified.

The expression for a single electrode potential in an oxidation-reduction cell is written:

$$E = E_0 + \frac{RT}{(m-n)F} \ln \frac{(M^+)}{(N^+)}$$

At this potential the gas equilibrium may be represented:

$$E = E'_0 + \frac{RT}{F} \ln \frac{(H^+)}{(H)} \quad \text{and} \quad E = E'_0 + \frac{RT}{2F} \ln \frac{(O)}{(O=)}$$

From these equations it is apparent that a definite hydrogen charge corresponds to a definite oxygen charge and that  $E$  increases with a rising concentration of the hydrogen ion. The ratio  $(O)/(O=)$  must increase with the rising concentration of the hydrogen ion. This explains the rise in potential of an oxidizing agent by the addition of a strong acid.

In the above equations it is to be noted that the author has used signs and ratios in the reverse to the now accepted conventions.

(1) Fredenhagen, Z. anorg. Chem., 29, 398 (1902).



The present theory of the hydrogen atom is based on the assumption that the electron is a particle of mass  $m$  and charge  $e$  moving in a circular orbit of radius  $r$  around a central nucleus of charge  $Ze$ . The electrostatic force of attraction between the electron and the nucleus is given by

$$F = \frac{Ze^2}{r^2} \quad (1)$$

where  $Z$  is the atomic number. The centrifugal force acting on the electron is given by

$$F = \frac{mv^2}{r} \quad (2)$$

where  $v$  is the velocity of the electron. For a stable orbit, the electrostatic force must be equal to the centrifugal force, i.e.,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r} \quad (3)$$

or

$$v^2 = \frac{Ze^2}{mr} \quad (4)$$

At this point, it is assumed that the angular momentum of the electron is quantized, i.e.,

$$mvr = n\hbar \quad (5)$$

where  $n$  is a positive integer and  $\hbar$  is the reduced Planck constant. Substituting equation (4) into equation (5), we get

$$r = \frac{n^2 \hbar^2}{Zme^2} \quad (6)$$

which gives the radius of the  $n$ th orbit. The total energy of the electron in the  $n$ th orbit is given by

$$E_n = -\frac{Z^2 e^4 m}{2n^2 \hbar^2} \quad (7)$$

where  $E_n$  is the energy of the electron in the  $n$ th orbit. This equation shows that the energy of the electron is quantized and depends on the principal quantum number  $n$ .



The potential of the reducing agent must obviously decrease under similar conditions. This explains the function of the acid in the oxidation-reduction reaction, and the improvement of the break in potentiometric work in the presence of a strong acid.

The magnitude of this break depends upon the difference in the value of  $E$  just prior to and just succeeding the equivalence-point. The effect of the acid is to increase this difference.

Willard and Fenwick carried out exhaustive research to support this theory.

It is evident that any difference in the electrode potential of unattackable electrodes will be due to difference in gas solubility. If, however, the electrodes are allowed to come to equilibrium with the solution, the potential will be the same irrespective of the electrode material. This was found to be true by using various electrodes in identical solutions of ferric/ferrous iron.

From the fact that pairs of unattackable electrodes had been used for titrations where a difference in electrode potential is necessary, it was suggested that it was the difference in the rate of assuming equilibrium of the different metals which was responsible for the difference in potential. The initial gas charge was varied on the electrodes by various methods of pre-treatment. The results while supporting the theory by showing different potentials in identical solutions, were too

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It is evident that any difference in the electrode potential of inert electrodes will be due to difference in the solubility. If, however, the electrodes are allowed to come to equilibrium with the solution, the potential will be the same in respect to the electrode material. This was found to be true by using various electrodes in identical solutions of ferric/ferrous ions.

From the fact that pairs of inert electrodes had been used for titrations where a difference in electrode potential is necessary, it was suggested that it was the difference in the rate of exchange equilibrium of the different ions which was responsible for the difference in potential. The initial rate of exchange was varied on the electrodes by various methods of treatment. The results, while not exactly in agreement with the theory, were too showing different potentials in identical solutions, were too



inconsistent to be of practical use in potentiometric titration work.

In order to use this difference in solubility of the gases in the metals, a method of reproducably keeping the electrodes out of equilibrium was necessary.

A system was devised consisting of two identical platinum electrodes made different in reaction by means of a small polarizing current. A current was drawn from a potential of .5 volts through a resistance of 100,000 ohms. This was found sufficient for the work. The current thus obtained was of the order of  $.5 \times 10^{-5}$  amperes, which is not large enough to cause error by electrolysis during the course of the titration.

It was first essential to study the individual electrode reaction under these conditions. A system was used consisting of a platinum electrode polarized by a small polarizing electrode, the potential of which could be measured against a standard half-cell.

Since the magnitude of the equivalence-point break is dependent upon the difference of the hydrogen charge just prior to the equivalence-point and the oxygen charge just succeeding the equivalence-point, it is apparent that either anodic or cathodic polarization will effect the desired increased magnitude in the break. The anodic polarization was found to be more suitable for the study of oxidation-reduction reactions since it increases the apparent strength of the oxidant, i.e. the oxygen charge. The reaction is carried out in a strongly



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In order to use this difference in solubility of the gases in the metals, a method of reproducibly keeping the electrodes out of equilibrium was necessary.

A system was devised consisting of two identical platinum electrodes made different in reaction by means of a small polarizing current. A current was drawn from a potential of 5 volts through a resistance of 100,000 ohms. This was found sufficient for the work. The current thus obtained was of the order of  $5 \times 10^{-5}$  amperes, which is not large enough to cause error by electrolysis during the course of the titration.

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acid medium and the hydrogen osmotic pressure is already increased by this means.

Platinum was found to be the best material for use in this work. Since even electrodes of apparently identically pure platinum were found to react differently, it is advised that the two electrodes be cut from one piece of material. It was shown that two pieces of pure platinum, analyzed by the Bureau of Standards, gave equivalence-point breaks of different magnitude. When both were cut from one piece, identical breaks were found, using one as cathode and the other as the anode and then reversing the polarity.

For use in titration work the parts are arranged as shown in Figure 10. The method of measuring the potential is the potentiometer circuit shown in Figure 5.

It should be noted that the only disadvantage of this system is the great localization of the equivalence-point change, the indication of which appears usually not more than .5 milliliters before the rather abrupt break at the equivalence-point.

The study of this system was followed up by the work of VanName and Fenwick. (1)

According to the theory the difference in potential between two non-identical electrodes is due to the difference in solubility of the gases in the electrodes. The difference

(1) R.G.VanName and F.Fenwick, J.Am.Chem.Soc., 47, 9 (1925)

(1) R. S. VanName and E. Tenzel, J. Am. Chem. Soc., 47, 2 (1925)

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can be measured only when the respective electrodes are out of equilibrium. According to this theory, then, the difference is really a time lag. If then the electrodes are allowed to remain in the solution, they should tend to assume the same potential.

This difference was measured as a function of time and the electrodes were actually found to tend to assume the same potential, the oxidation-reduction potential for that concentration of the reactants.

The behavior of the bimetallic system can be more accurately studied when the artificially polarized system is used, the two platinum electrodes made different in reaction by means of a small polarizing current, since in this system, the measurements are reproducible. This system was used to study the phenomenon of the break at the equivalence-point.

It was found that the principal factor in determining the sharpness of the potentiometric equivalence-point is the difference in degree of reversibility of the electrode reaction before and after the equivalence-point.

As a specific example the reaction of ferrous iron with potassium permanganate was studied.

When this reaction is started only ferrous iron is present and there is a difference in potential due to the depolarization of the anode. After the first addition of the oxidant, there is present both ferrous and ferric ions and both of the electrodes are depolarized. There is now little or no differ-

can be measured only when the respective electrodes are out of equilibrium. According to this theory, then, the difference is really a time lag. If then the electrodes are allowed to remain in the solution, they should tend to assume the same potential.

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The behavior of the bimetallic system can be more accurately studied when the artificially polarized system is used. The two platinum electrodes made different in reaction by means of a small polarizing current, since in this system, the measurements are reproducible. This system was used to study the phenomenon of the break at the equivalence-point.

It was found that the principal factor in determining the sharpness of the potentiometric equivalence-point is the difference in degree of reversibility of the electrode reaction before and after the equivalence-point.

As a specific example the reaction of ferrous iron with potassium permanganate was studied.

When this reaction is started only ferrous iron is present and there is a difference in potential due to the depolarization of the anode. After the first addition of the oxidant, there is present both ferrous and ferric ions and both of the electrodes are depolarized. There is now little or no differ-



ence in potential between the electrodes. At the equivalence-point the ferrous ion disappears and the permanganate ion appears. The potentials of the electrodes rise sharply but by different amounts. At this higher potential the depolarizing effect of the ferric ion is too weak to be felt, so at the equivalence-point and just beyond neither electrode is effectively depolarized.

By studying the system containing also the half-cell, the potential on both the cathode and the anode could be followed. Figure 11. shows typical curves. By similar studies with other reactions, the applicability of this system for that particular reaction could be determined.

It was discovered that, in the use of polarized electrodes, one of the electrodes in some cases came to a change a little before or a little after the equivalence-point. This did not affect the maximum difference between the two electrodes enough to cause error in the results of the titration.

A study of the effect of the rate of stirring showed that the efficiency of the depolarization depended upon the efficiency of the stirring. This is a minor factor and ordinarily efficient stirring was found to be satisfactory.

All of the experimental work to this point has concerned oxidation-reduction reactions.

A bimetallic system was tried in the titration of silver with chloride. Various results were found, but when an equivalence-point break was observed the electrode seemed to

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# THE POLARIZED PLATINUM ELECTRODE SYSTEM OF WILLARD AND FENWICK

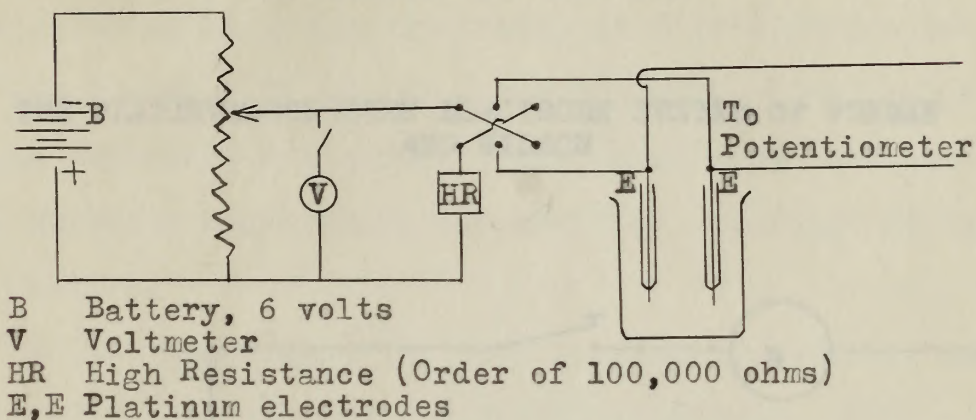


Figure 10.

## POTENTIAL ON THE POLARIZED PLATINUM ELECTRODES

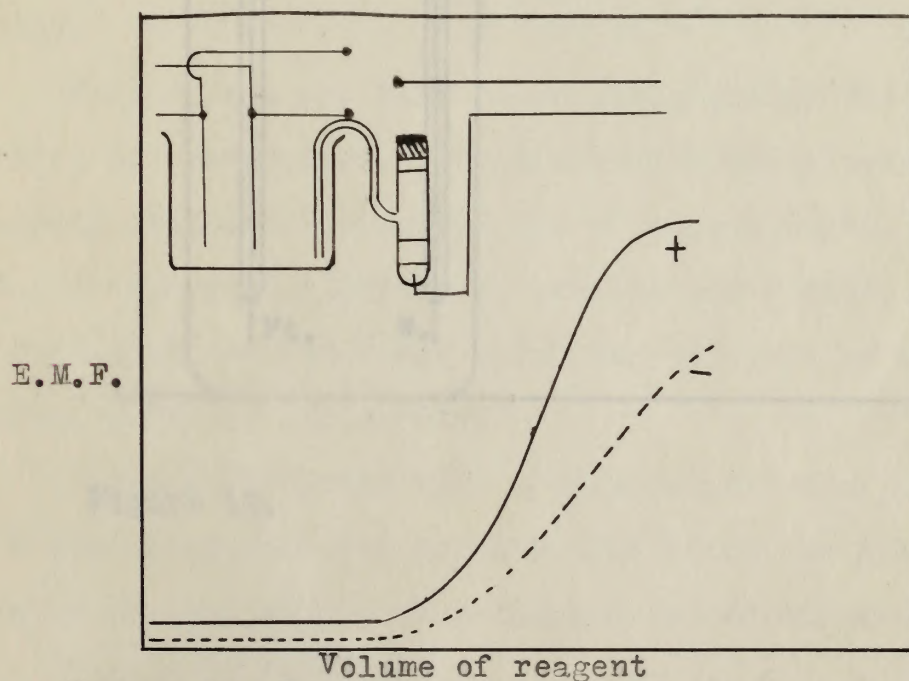


Figure 11. Including the method of measuring the individual electrode potentials.

# THE POLARIZED PLATINUM ELECTRODE SYSTEM OF WILLARD AND FERNICK

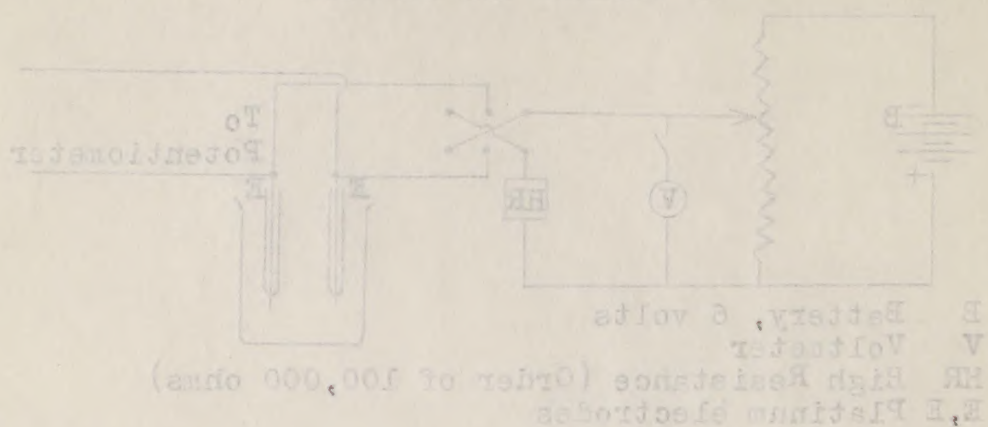


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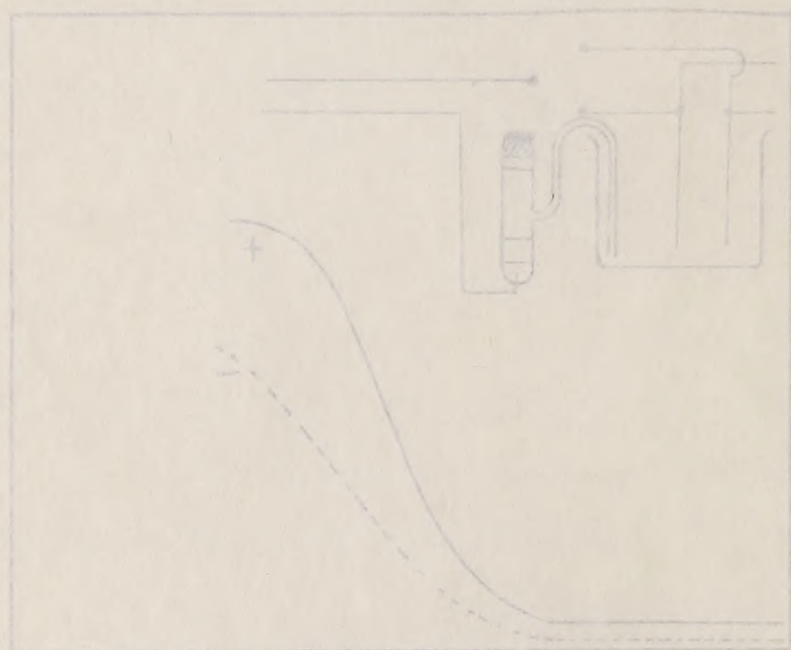


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# THE PLATINUM-TUNGSTEN ELECTRODE SYSTEM OF FURMAN AND WILSON

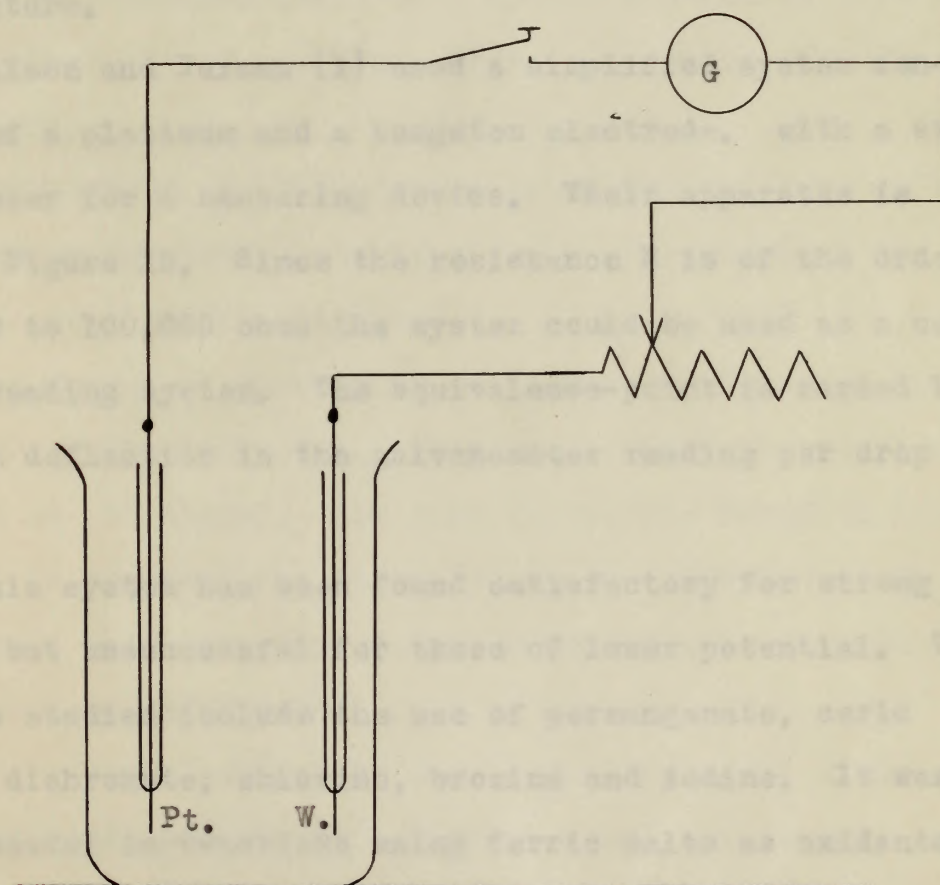


Figure 12.

- (1) H. E. Furman and E. E. Wilson, Jr., J. Am. Chem. Soc., 50, 277 (1928)
- (2) H. E. Furman, J. Am. Chem. Soc., 50, 272 (1928)

THE PLATINUM-TUNGSTEN ELECTRODE SYSTEM OF WILSON  
AND WILSON

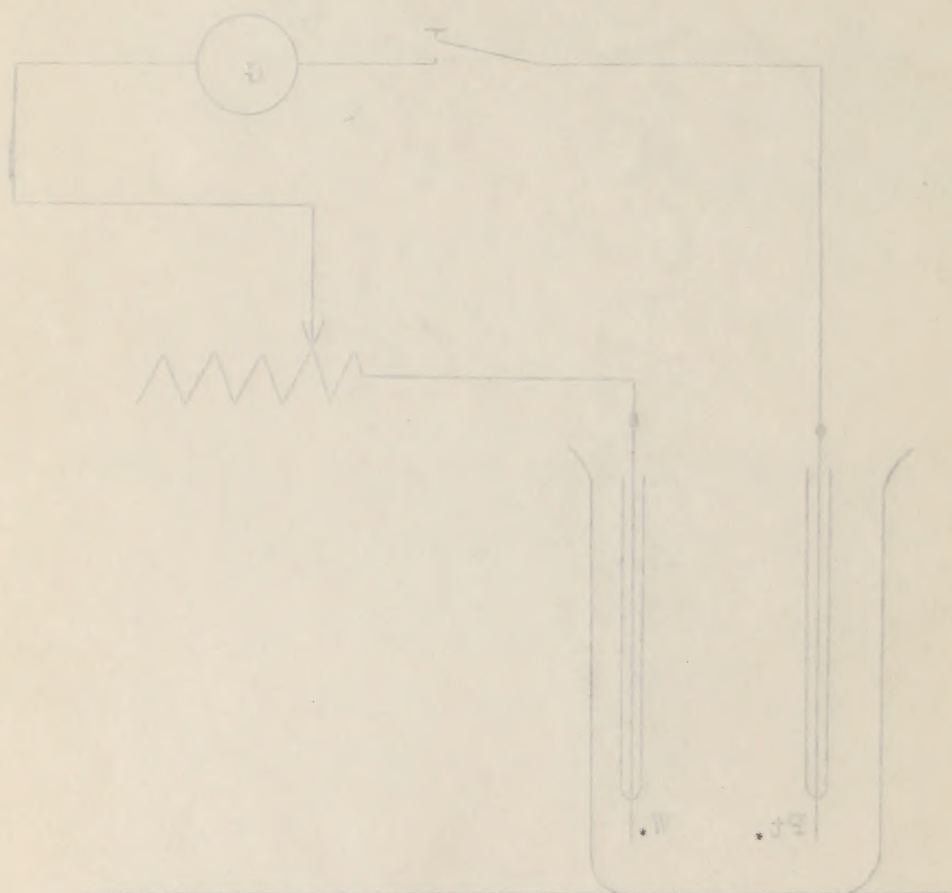


Figure 18.



act as a silver electrode.

Using the polarized platinum electrodes system in the titration of an acid-base reaction, no equivalence-point break was found. By adding a small amount of neutralized hydrogen peroxide, the solution was transformed into an oxidizing solution and a break was observed, although of temporary nature.

Wilson and Furman (1) used a simplified system consisting of a platinum and a tungsten electrode, with a simple galvanometer for a measuring device. Their apparatus is shown in Figure 12. Since the resistance  $R$  is of the order of 10,000 to 100,000 ohms the system could be used as a continuous reading system. The equivalence-point is marked by a maximum deflection in the galvanometer reading per drop of reagent.

This system has been found satisfactory for strong oxidants but unsuccessful for those of lower potential. The reactions studied include the use of permanganate, ceric sulfate, dichromate, chlorine, bromine and iodine. It was not successful in reactions using ferric salts as oxidants or titanous salts as reductants.

Furman (2) found that system comprised of a platinum and a gold electrode was suitable for titration potentiometrically of iron with both permanganate and dichromate.

- (1) N.H.Furman and E.B.Wilson, Jr., J. Am. Chem. Soc., 50, 277 (1928)  
(2) N.H.Furman, J. Am. Chem. Soc., 50, 273 (1928)

(1) N. H. Furman, J. Am. Chem. Soc., 50, 268 (1928)

not as a silver electrode. Using the polarized platinum electrode system in the titration of an acid-base reaction, no equivalence-point break was found. By adding a small amount of neutralized hydrogen peroxide, the solution was transformed into an oxidizing solution and a break was observed, although of fairly poor nature.

Wilson and Furman (1) used a simplified system consisting of a platinum and a tungsten electrode, with a simple galvanometer for a measuring device. Their apparatus is shown in Figure 12. Since the resistance R is of the order of 10,000 to 100,000 ohms the system could be used as a continuous reading system. The equivalence-point is marked by a maximum deflection in the galvanometer reading per drop of reagent.

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It was found effective for solutions as dilute as .05 normal.

The metallic electrode system consisting of platinum and gold amalgam electrodes was found by Furman (1) to be satisfactory for the titration of various oxidation-reduction reactions. The gold amalgam electrode was found to behave similarly to a calomel cell, in a system containing chlorine ions and similarly to a sulfate cell in a system containing sulfate ions.

The E. M. F. in this system is nearly the same as the corresponding mercurous salt half-cell. The shape of the titration curve is also similar.

The amount of mercury on the electrode does not appreciably affect the titration. This was studied in solutions as dilute as .05 normal. The time factor was found to have no effect in changing the potential on the electrode. It is evident that this metallic electrode really acts as a half-cell and not as a gas electrode.

The systems studied by this method include: dichromate-ferrous sulfate; permanganate-ferrous iron; and vanadic acid-ferrous sulfate. From preliminary observation the system can also be used for the titration of neutralization reactions, involving hydrochloric and sulfuric acids, and also for precipitation reactions where either of these ions is present.

The amalgam electrode is fairly simple to prepare. An electrode consisting of a small piece of gold wire sealed into (1) N. H. Furman, J. Am. Chem. Soc., 50, 268 (1928)



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(1) W. R. Larnan, J. Am. Chem. Soc., 50, 268 (1928)



glass, is dipped momentarily into pure mercury. The electrode is kept in dilute hydrochloric acid when not in use, as exposure to air will cause it to become sluggish.

The bimetallic electrode systems and the polarized platinum system have been found very satisfactory for use in most oxidation-reduction systems. For use in the titration of acids and bases the results are not always so easily obtained in the methods presented so far. There has been much research in the use of the metallic systems for neutralization reactions.

A system similar to that of Dutoit and vonWeisse(1) was devised by Wright and Gibson (2) to be used for the titration of acids and bases. The electrode system consists of a calomel half-cell and an indicator electrode of platinum polarized cathodically by an auxillary platinum electrode. They used a polarizing current from a potential of 2 volts through a resistance of 500,000 ohms. They presented data only for solutions of .5 normal strength. The equivalence-point break came close to a zero potential between the electrodes, but the titration curve was typical in form.

The use of antimony as an indicator electrode has been studied extensively for use in pH determinations and for neutralizations and found very satisfactory. (3)

Franke and Williaman (4) experimented with several anti-

- (1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.
- (2) A.H.Wright and F.H.Gibson, Ind.Eng.Chem. 19, 749 (1927).
- (3) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 235.
- (4) K.W.Franke and J.J.Williaman, Ind.Eng.Chem., 20 87 (1928).



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- (2) A.H. Wright and T.R. Gibson, Ind. Eng. Chem., 19, 749 (1927).
- (3) Cf. Potentiometric Titrations, Kolthoff-Irman, p. 235.
- (4) R.W. Frank and J.T. Williamson, Ind. Eng. Chem., 30 87 (1938).



mony electrodes. They found best results from pure stick antimony, 7 millimeters in diameter and 40 to 50 millimeters in length, which had been filed and rubbed smooth. The equation for the potential for this electrode is:

$$E = .050 + .054\text{pH} \quad \text{at 25 degree centigrade.}$$

This holds over the pH range from 0 to 12.

The presence of oxygen or carbon dioxide was found to cause a drift in the potential reading. Medium stirring is recommended. The advantage of the antimony electrode over the quinhydrone electrode lies in its effective use over a longer pH range.

After experimenting with various combinations, Brunnich (1) found that an electrode system consisting of pure graphite and platinum was satisfactory for the titration of neutralization reactions. The electrode must be of the purest graphite. A method of testing the electrode before use was suggested. Measure the potential on the electrode in pure water, in which the potential should be zero. Follow this test by determining its potential in pure water containing a drop of acid and in pure water containing a drop of alkali. The equivalence-point of this system is found very close to the zero potential.

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accurate titrations in the following methods: Platinum and a calomel cell; a differential system using platinum electrodes in two beakers connected by a salt bridge, similar to the system of Cox (1); a concentration cell, one half of which at the pH of the equivalence-point of the reaction; and a platinum and graphite system similar to that of Brunnich. In the use of the platinum-graphite system an irregular curve was found but a very accurate break was characteristic.

A system consisting of antimony and copper amalgam electrodes was found effective in neutralization titrations by Fuoss. (2) He also studied the systems: antimony-lead; bismuth-silver; and copper-copper oxide. The antimony-copper amalgam system was found to be the best of this group.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 112.  
(2) R. M. Fuoss, Ind. Eng. Chem. Analyt. Ed., 1, 125 (1929).







## NOTE

Willard and Fenwick have applied their polarized platinum electrode system to several volumetric reactions which have not been mentioned in the explanation of their system. (1)

They found their system successful in the titration of an iodide with permanganate in the presence of HCN. In the titration of a bromide, however, the results were not satisfactory. (2)

The polarized platinum electrode system was found satisfactory for the reaction involving an iodate with a thiocyanate in the presence of HCl. (3)

In the titration of ferrous iron with a bromate in an acid medium only fair results were obtained. (3)

The estimation of zinc with ferrocyanide, using this system was found to be only fairly satisfactory. (3)

Good results were obtained in the titration of vanadate with ferrous iron. (2)

The titration of arsenic trioxide with hypochlorite is also successful with this system of electrodes. (3)

An unsuccessful attempt was made to titrated an iodide with a hypobromite. (3)

Titanium salts were used in the estimation of copper and of selenium with success by this system. (2)

(1) Cf. This thesis, p. 37.

(2) Willard, H.H. and Fenwick, F, J. Am. Chem. Soc., 45, (1923)

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(1) H.H. Willard and F. Fenwick, J. Am. Chem. Soc., 45, 928, (1923)

(2) H.H. Willard and E.P. Wilson, Jr., J. Am. Chem. Soc., 50, 275 (1928)

50

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(1) H.H. Willard and F. Renwick, J. Am. Chem. Soc., 45, 922 (1923)



## V. CONTINUOUS READING DEVICES.

In the determination of the potential, the essential problem is to measure the voltage without taking from the system an appreciable amount of current.

The application of the potentiometer is very successful for this purpose. For detailed study of the course of the reaction, it is the simplest system. For general work, although it is effecient, it has the disadvantage of necessitating the constant tapping of a key and balancing of the circuit. Much work has been done to find a simple system, which would fulfill the requirement of drawing little current, yet eliminate the tapping key and the constant balancing and in some cases to eliminate the plotting of a graph in order to determine the equivalence-point of a reaction.

The simplest method of measuring voltage would be to connect a voltmeter between the electrodes. This necessitates the passage of current. Furman and Wilson, in their system using tungsten and platinum, have a simple continuous reading system, using a galvanometer instead of a voltmeter. The system is protected from the passage of an appreciable amount of current by placing in the circuit a high resistance. (1)

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(1) K.H. Furman and E.B. Wilson, Jr., J. Am. Chem. Soc., 50, 277 (1928)



vanometer. This method was devised by Faulk and Bawden (1), who call this system "Galvanometry".

Figure 13. shows the diagram of their apparatus.

They first found successful operation of this type of apparatus with iodine-arsenite or thiosulfate reactions.

This system is really a modification of the polarized platinum electrode system of Willard and Fenwick. (2) It introduced a new principle in the shunting of the electrodes. The two electrodes are polarized by a potential of about 10 to 15 millivolts, small enough so that the polarizing back E.M.F. balances it and there is no passage of current through the electrodes.

The success of this type of apparatus depends upon the effective depolarizing power of the reactants and the resultants of the reaction.

It can be used in any one of the following instances:

1. One electrode is polarized during the titration. The reacting solution must depolarize this electrode, when it is present in the slightest excess, at the equivalence-point. This is the case when a thiosulfate or arsenite solution is titrated with iodine. The reducing solution, present throughout the titration, thiosulfate or arsenite before the equivalence-point and the iodide after the equivalence-point, keep the anode depolarized. When the iodine excess is first apparent, the ca-

(1) C.W.Faulk and A.T.Bawden, J.Am.Chem.Soc., 48, 2045 (1926)

(2) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 44, 2516 (1922)



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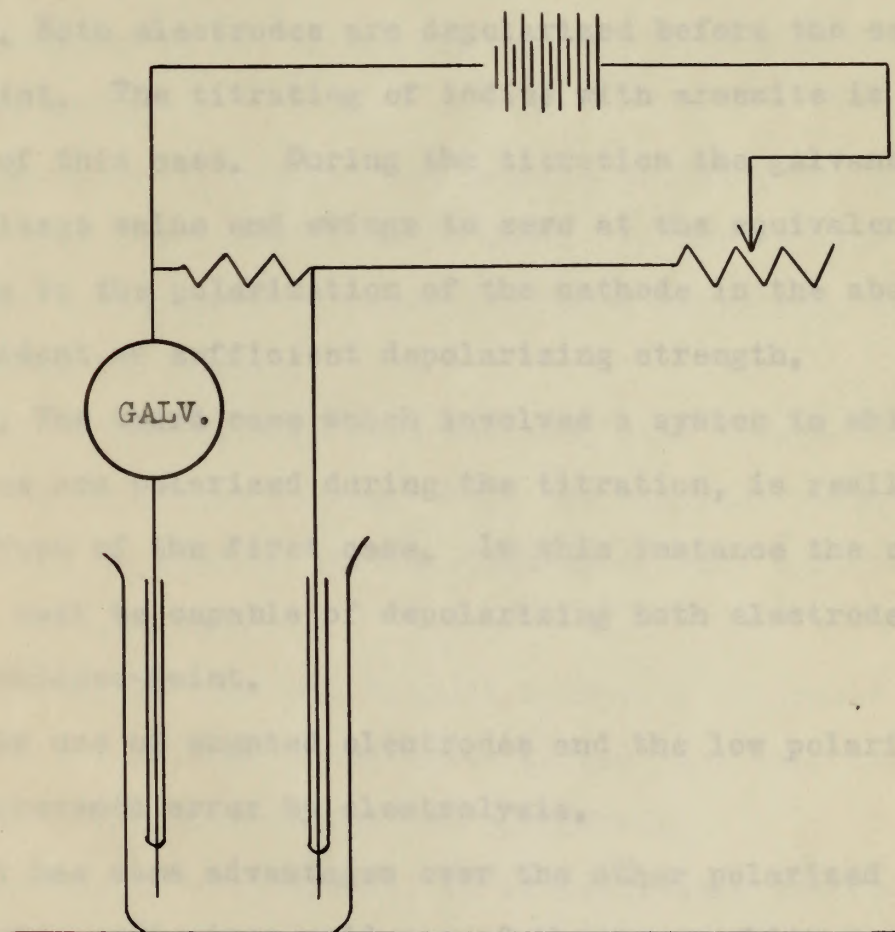


Figure 13. #Note shunted electrodes.

THE POLARIZED PLATINUM ELECTRODE  
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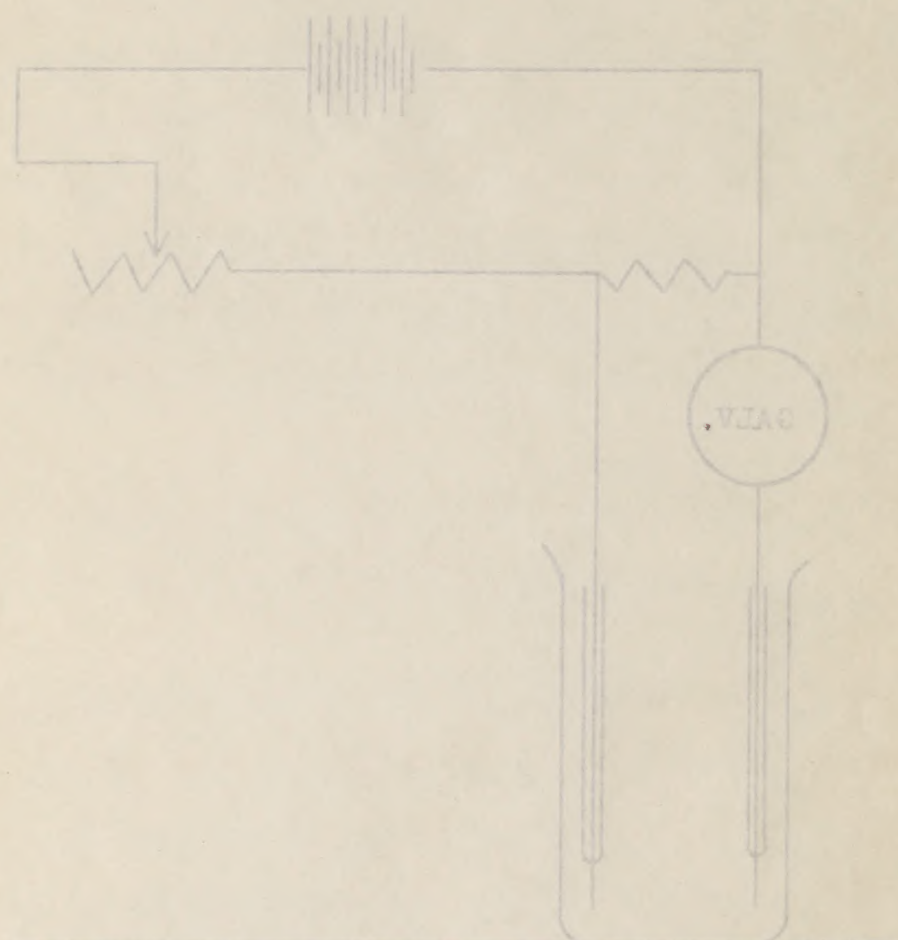


Figure 18. Photo mounted electrodes.



thode is depolarized. At the equivalence-point, both electrodes being depolarized, current is allowed to flow and the galvanometer needle is permanently displaced. Throughout the titration the galvanometer reads zero until near the equivalence-point when temporary deflections are noted.

2. Both electrodes are depolarized before the equivalence-point. The titrating of iodine with arsenite is an example of this case. During the titration the galvanometer reads a large value and swings to zero at the equivalence-point due to the polarization of the cathode in the absence of an oxidant of sufficient depolarizing strength.

3. The third case which involves a system in which both electrodes are polarized during the titration, is really a special form of the first case. In this instance the reacting solution must be capable of depolarizing both electrodes at the equivalence-point.

The use of shunted electrodes and the low polarizing current prevents error by electrolysis.

It has some advantages over the other polarized electrode system. It gives evidence of the approaching equivalence-point by temporary swings of the galvanometer needle. Over-titration is at once apparent.

This system was also found successful for permanganate titration of oxalate.

The use of the electron tube circuits for potential measurements has developed greatly in the past few years, main-



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ly in connection with the work in radio and general electrical experimenting.

This type of apparatus has been found successful for use in potentiometric titrations, because the characteristics of this method of measuring potential fit perfectly the essentials necessary to the measurement of the potential of the titration cell.

There are in general two methods of using the electron tube circuits for potentiometric work. It may be used for continuous measurement of potential, as a voltmeter, or as a null-point instrument.

Many circuits have been devised, some simple and some of a very complicated nature. Only the simplest examples illustrating in general the functioning of this type of apparatus will be presented.

For use of the tube circuit both as a voltmeter and as a null-point instrument, the basis is the fact that the plate current is a function of the grid potential.

For use as a voltmeter, it is desirable to have the plate current a linear function of the grid potential. In any case the characteristics of the electron tube must be known.

Goode (1) was the first to devise a method of applying this type of circuit to potentiometric titrations. His circuit is shown in Figure 14.

(1) K. H. Goode, J. Am. Chem. Soc., 44, 26, (1920)



ly in connection with the work in radio and general electrical experimenting.

This type of apparatus has been found successful for use in potentiometric titrations, because the characteristics of this method of measuring potential fit perfectly the essential necessary to the measurement of the potential of the titration cell.

There are in general two methods of using the electron tube circuits for potentiometric work. It may be used for continuous measurement of potential, as a voltmeter, or as a null-point instrument.

Many circuits have been devised, some simple and some of a very complicated nature. Only the simplest examples illustrating in general the functioning of this type of apparatus will be presented.

For use of the tube circuit both as a voltmeter and as a null-point instrument, the basis is the fact that the plate current is a function of the grid potential.

For use as a voltmeter, it is desirable to have the plate current a linear function of the grid potential. In any case the characteristics of the electron tube must be known.

Goode (1) was the first to devise a method of applying this type of circuit to potentiometric titrations. His circuit is shown in Figure 1A.

(1) K. H. Goode, J. Am. Chem. Soc., 44, 36, (1922)



In his apparatus the change in potential of the titration cell, between the electrodes, is applied on the grid of the electron tube. The effect of the change in grid potential is amplified in the plate current. The plate current, which is a known function of the grid potential is read on a large sensitive galvanometer.

He later modified his apparatus to include three tubes, making the reading more sensitive by the added amplification.(1)

Many other voltmeter circuits have been devised all based on the known function of the plate current in the grid potential. The current necessary to charge the grid is so small that there is no error due to electrolysis in the titration cell. The advantage gained by the elimination of the tapping key and the balancing of the circuit is obvious.

In the null-point circuits the electron tube circuit functions as a galvanometer. Figure 15. shows a typical circuit. The method shown was devised by Partridge. (2)

For operation the switch S is placed in position n. The circuit is now functioning without the effect of the cell to be measured, which is connected at E. The circuit is so balanced that MA, a sensitive milliammeter reads a definite but arbitrary value, taken at the center of the scale for convenience. To read the voltage on E, the switch is changed to the position m. The resistance R is varied until MA reads the same

- (1) K. H. Goode, J. Am. Chem. Soc., 47, 2483 (1925)  
(2) H. M. Partridge, J. Am. Chem. Soc., 51, 1 (1929)



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In the null-point circuit the electron tube circuit functions as a galvanometer. Figure 15, shows a typical circuit. The method shown was devised by Partridge. (2)

For operation the switch S is placed in position 1. The

circuit is now functioning without the effect of the cell to be measured, which is connected at E. The circuit is so balanced that MA, a sensitive milliammeter reads a definite but arbitrary value, taken at the center of the scale for convenience. To read the voltage on E, the switch is changed to the position 2. The resistance R is varied until MA reads the same

(1) K. H. Geode, J. Am. Chem. Soc., 47, 2483 (1925)  
(2) H. W. Partridge, J. Am. Chem. Soc., 51, 1 (1929)



### GOODE'S CONTINUOUS-READING APPARATUS

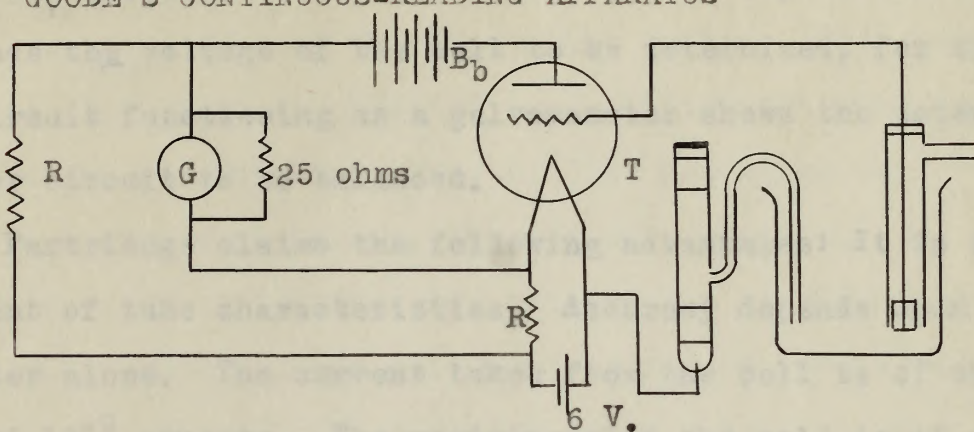


Figure 14.

### PARTRIDGE'S APPARATUS

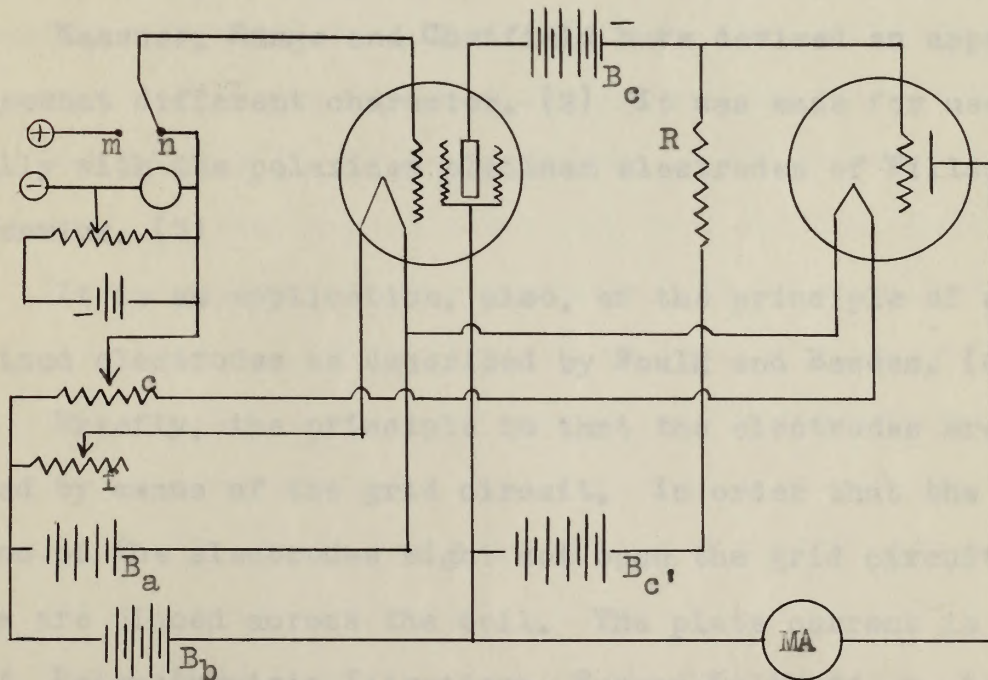


Figure 15.

Figure 14. PARALLEL-READING APPARATUS

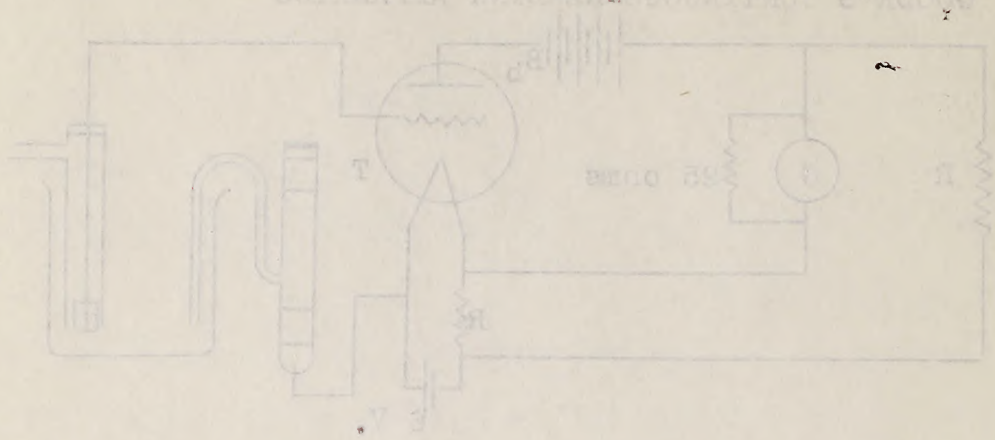


Figure 15. PARALLEL-READING APPARATUS

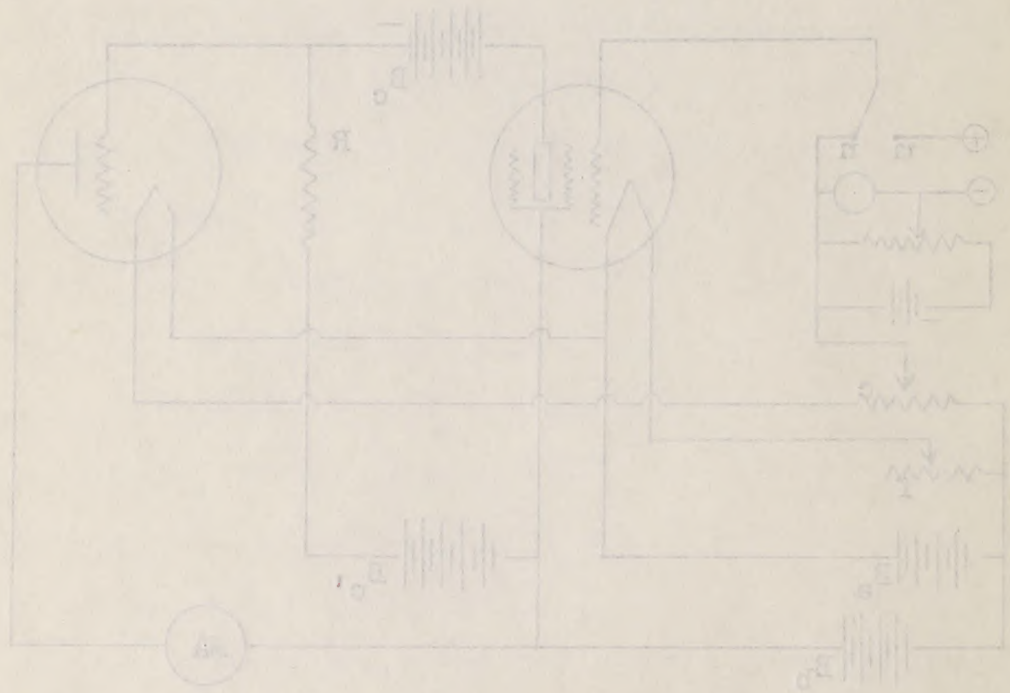


Figure 16. PARALLEL-READING APPARATUS



as on open circuit. When this condition exists, the voltmeter reads the voltage of the cell to be determined, for the tube circuit functioning as a galvanometer shows the potentiometer circuit to be balanced.

Partridge claims the following advantages: It is independent of tube characteristics. Accuracy depends upon the voltmeter alone. The current taken from the cell is of the order of  $10^{-9}$  amperes. The resistance of the cell is of no importance. This system is especially adapted to use with the glass electrode.

Several other circuits have been devised in which the circuit acts as a galvanometer. In general their characteristics are similar. (1)

Kassner, Hunge and Chatfield have devised an apparatus of somewhat different character. (2) It was made for use especially with the polarized platinum electrodes of Willard and Fenwick. (3)

It is an application, also, of the principle of shunted polarized electrodes as described by Foulk and Bawden. (4)

Briefly, the principle is that the electrodes are polarized by means of the grid circuit. In order that the polarization of the electrodes might not open the grid circuit, shunts are placed across the cell. The plate current is

(1) Cf. Potentiometric Titrations, Furman-Kolthoff, p. 134.

(2) J.Kassner, R.Hunge and N.Chatfield, J.Am.Chem.Soc., 54, 2279 (1932)

(3) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 44, 2516 (1922)

(4) C.W.Foulk and A.T.Bawden, J.Am.Chem.Soc., 48, 2045 (1926)



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- (3) R. H. Willard and E. Fenwick, J. Am. Chem. Soc., 44, 3516 (1922).
- (4) C. W. Foulk and A. T. Bowden, J. Am. Chem. Soc., 48, 3045 (1926).



balanced against the filament circuit through the galvanometer. This is really a form of the Wheatstone bridge. This type of apparatus is especially adapted to the titration characteristics of the polarized electrodes. For operation the galvanometer is balanced to zero by the variable resistance R. Since there is no potential difference between the electrodes up to the equivalence-point, the galvanometer should read zero during the titration and have a sudden maximum deflection at the equivalence-point.

In practice, the galvanometer reading during the titration is slightly different from that described above. At the beginning the reading is balanced to zero. As the titration continues the needle swings gradually to the right. As the equivalence-point is approached there are temporary kicks to the left and at the exact equivalence-point the needle swings permanently to the left extreme. The indication of the approach to the equivalence-point is a decided advantage.

It has various other advantages. It is characterized by high sensitivity. Overtitrating is instantly indicated. In this system the plotting of curves is unnecessary to determine the equivalence-point. The characteristics of the tube are unessential. Adjustments during the titration are unnecessary. It is truly continuous reading.

The untheoretical reading on the galvanometer and the kicks indicating the approach to the equivalence-point are procured by a unique placing of the electrodes, which causes



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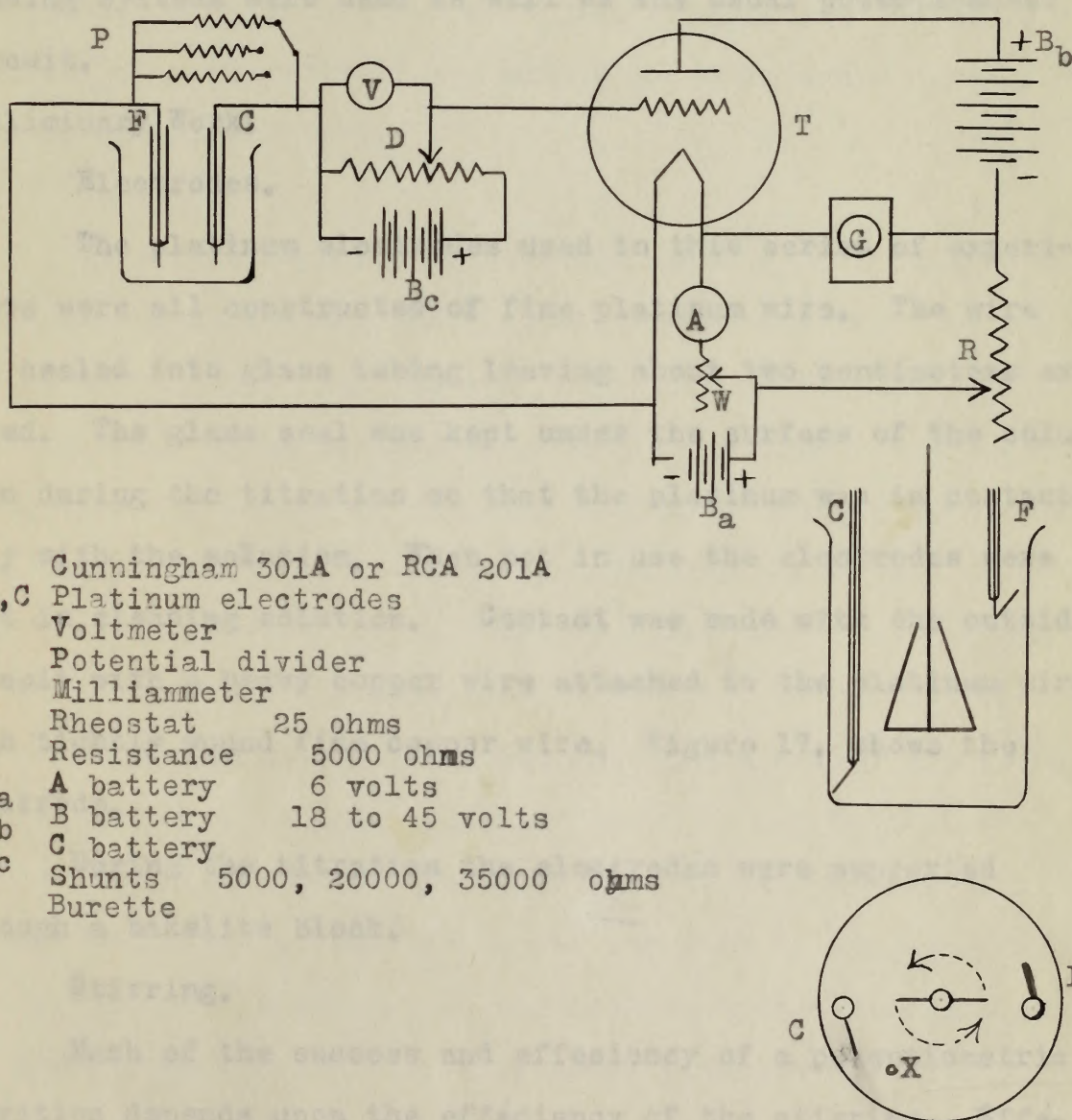
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a slight difference in the rate at which the electrodes come to equilibrium throughout the titration.

The apparatus and the method of placing the electrodes is shown in figure 16.

#### APPARATUS OF KASSNER, HUNGE AND CHATFIELD



- T Cunningham 301A or RCA 201A
- F, C Platinum electrodes
- V Voltmeter
- D Potential divider
- A Milliammeter
- W Rheostat 25 ohms
- R Resistance 5000 ohms
- $B_a$  A battery 6 volts
- $B_b$  B battery 18 to 45 volts
- $B_c$  C battery
- $P^c$  Shunts 5000, 20000, 35000 ohms
- X Burette

Figure 16.





## VI. EXPERIMENTAL RESULTS.

Experiments were conducted, using several of the methods involving platinum electrodes, with a view to determining their applicability to ordinary laboratory procedures. Continuous reading systems were used as well as the usual potentiometer circuit.

### Preliminary Work.

#### Electrodes.

The platinum electrodes used in this series of experiments were all constructed of fine platinum wire. The wire was sealed into glass tubing leaving about two centimeters exposed. The glass seal was kept under the surface of the solution during the titration so that the platinum was in contact only with the solution. When not in use the electrodes were kept in cleaning solution. Contact was made with the outside circuit with a heavy copper wire attached to the platinum wire with tightly wound fine copper wire. Figure 17. shows the electrode.

During the titration the electrodes were supported through a bakelite block.

#### Stirring.

Much of the success and efficiency of a potentiometric titration depends upon the efficiency of the stirring. Efficient stirring brings the reaction to equilibrium sooner as well as the electrode reaction.

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During the titration the electrodes were supported through a bakelite block.

Stirring.

Much of the success and efficiency of a potentiometric titration depends upon the efficiency of the stirring. Efficient stirring brings the reaction to equilibrium sooner as well as the electrode reaction.



The apparatus was arranged so that the solution could be stirred by a glass stirrer revolved by an electric motor.

This glass stirrer usually consists simply of a bent glass rod. In order to make the stirring more effecient, an agitator was made with glass rod similar to the diagram in Figure 18. It was found to work very well and caused no splash-  
ing even when the ends of the agitator arm extended above the surface of the solution.

#### Burette.

The titration chamber consists usually of a beaker, into which extend electrodes and a motor driven stirrer. The tip of the burette must also extend in to just above the level of the solution. When the reaction must be carried out in an inert atmosphere the beaker is replaced by a wide mouthed vessel of some type, which can be closed tightly with a stopper. All of the apparatus must extend through this stopper as well as the inlet tube for the inert gas.

For convenience a burette was made similar in structure to the burette electrode shown in Figure 7, but without the sealed-in platinum wire. Both the burette and the stopcock by this means are out of the way of the rest of the apparatus in the titration chamber. It was found too that this electrode was convenient for ordinary titrations in which the reaction must be kept hot.

#### Calibrations.

All burettes, pipettes and flasks were accurately



The apparatus was arranged so that the reaction could

be followed by a glass mirror revolved by an electric motor.

This glass mirror usually consists of a disk

of glass. In order to make the rotating more efficient, an

aluminum was added with glass not similar to the mirror in

figure 1. It was found to work very well and caused no splash-

ing even when the ends of the mirror are extended above the

surface of the solution.

Results.

The reaction chamber consists usually of a beaker, into

which extend electrodes and a motor driven stirrer. The tip

of the burette also extends in it just above the level of

the solution. When the reaction was carried out in an inert

atmosphere the beaker is replaced by a dry, sealed vessel of

some type, which can be closed tightly with a stopper. All

of the apparatus was kept dry and oxygen free throughout the experiment.

The electrodes for the reaction were

for convenience a burette was used as a cathode and a platinum

rod as the anode. Electrodes were in figure 2, but without the

beaker in place. Both the burette and the electrode

by this means are out of the way of the rest of the apparatus

in a reaction chamber. It was found that this electrode

was convenient for ordinary reactions in which the reaction

must be kept hot.

Conclusions.

All reactions, electrodes and flasks were completely



PLATINUM ELECTRODE

STIRRER

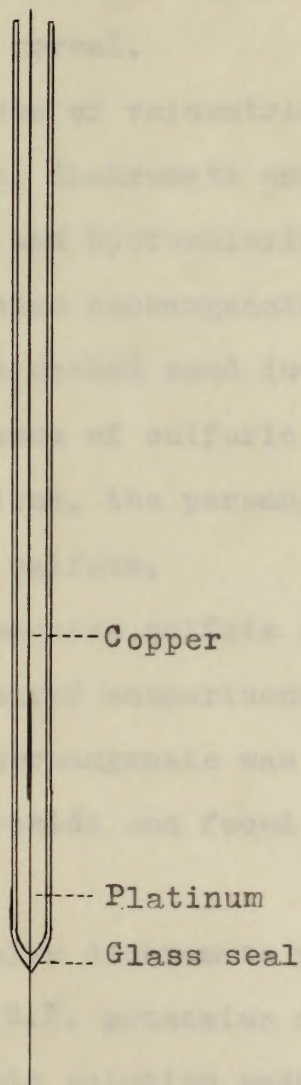


Figure 17.

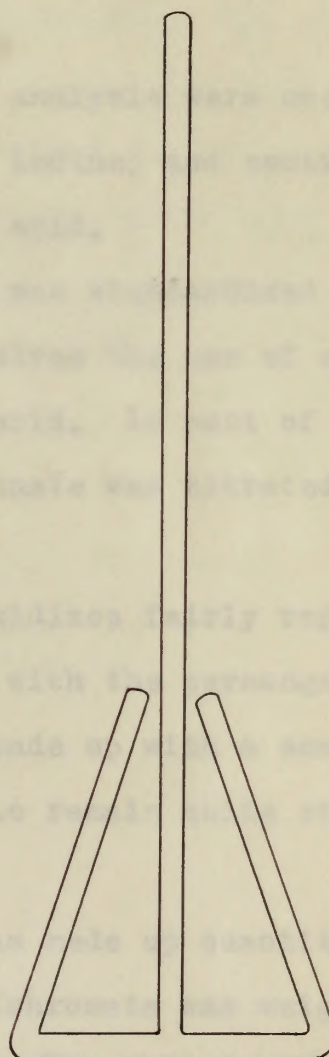


Figure 18.



Figure 16.

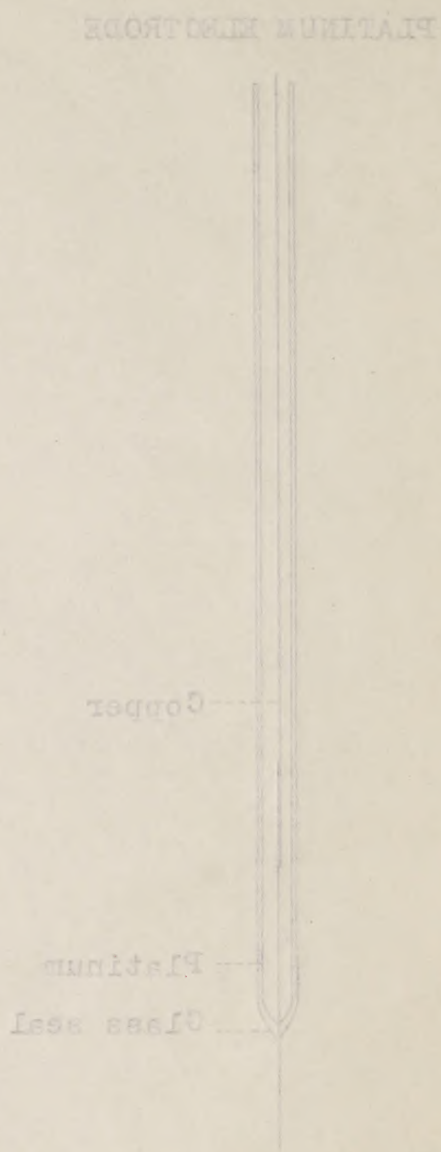


Figure 17.



calibrated before use.

### Solutions.

All solutions used in this series of experiments were approximately .1 normal.

Four systems of volumetric analysis were used: oxidations with permanganate, dichromate and iodine; and neutralization, sodium hydroxide and hydrochloric acid.

The potassium permanganate was standardized against sodium oxalate. The method used involves the use of a hot titration in the presence of sulfuric acid. In most of the potentiometric titrations, the permanganate was titrated against ferrous ammonium sulfate.

Ferrous ammonium sulfate oxidizes fairly rapidly on standing and repeated comparisons with the permanganate were necessary. The permanganate was made up with a small amount of potassium hydroxide and found to remain quite stable over several months.

The potassium dichromate was made up quantitatively. Ground and dried C.P. potassium dichromate was weighed accurately and a volumetric solution made. The solution was then compared with a ferrous ammonium sulfate solution which had been just titrated with permanganate. The normality thus determined was the same as the value calculated from the amount weighed.

The iodine in potassium iodide solution was standardized

calibrated before use.

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termined was the same as the value calculated from the amount

weighed.

The iodine in potassium iodide solution was standardized



against arsenious oxide. Sodium thiosulfate was usually used with the iodine in the potentiometric titrations.

In the neutralization reaction the hydrochloric acid was standardized against sodium carbonate. The normality of the sodium hydroxide was found by comparison with the acid.

All solutions were standardized and compared colorimetrically before being used for potentiometric work.

The following table shows the results obtained in the titration of arsenious oxide with potassium permanganate. The volume of the arsenious solution was placed in the beaker with the indicator and the volume of water and 20 milliliters of concentrated sulfuric acid.

The following table shows the results obtained.

No. of Fe	Vol. of $K_2Cr_2O_7$		Vol. of $K_2Cr_2O_7$	Vol. of $K_2Cr_2O_7$
	Initial	Final	Initial	Final
I. 20.00	21.00	21.25	20.00	20.00
II. 20.00	21.00	21.25	20.00	20.00
III. 20.00	21.00	21.25	20.00	20.00
IV. 20.00	21.00	21.25	20.00	20.00

The results show this method to be accurate for this titration within the limits of experimental error. It is significant that one drop of potassium permanganate over the potentiometric end-point gave the colorimetric end-point.

Figure 12, shows a titration curve for this titration.

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In the neutralization reaction the hydrochloric acid was standardized against sodium carbonate. The normality of the sodium hydroxide was found by comparison with the acid. All solutions were standardized and compared colorimetrically before being used for potentiometric work.



# Polarized Platinum Electrode System of Willard and Fenwick.(1)

The apparatus was set up as is shown diagrammatically in Figure 10. The current was drawn from a potential of .5 volts through a resistance of 100,000 ohms. The polarizing current was, then, of the order of  $.5 \times 10^{-5}$  amperes. This arrangement was found satisfactory for the reactions studied.

The first reaction studied was the titration of ferrous ammonium sulfate with potassium permanganate. 24.96 milliliters of the ferrous solution was placed in the beaker with 250 milliliters of water and 10 milliliters of concentrated sulfuric acid.

The following tabulation shows the results obtained.

	Ml. of Fe	Ml. of $\text{KMnO}_4$		error	Magnitude of break-mv.
		calc'd	found		
I.	24.96	21.96	21.95	-.01	440
	24.96	21.96	21.98	.02	440
II.	24.96	20.75	20.75	.00	380
	24.96	20.75	20.75	.00	440

The results show this method to be accurate for this titration within the limits of experimental error. It is significant that one drop of permanganate over the potentiometric equivalence-point gave the colorimetric end-point.

Figure 19. shows a titration curve for this titration.

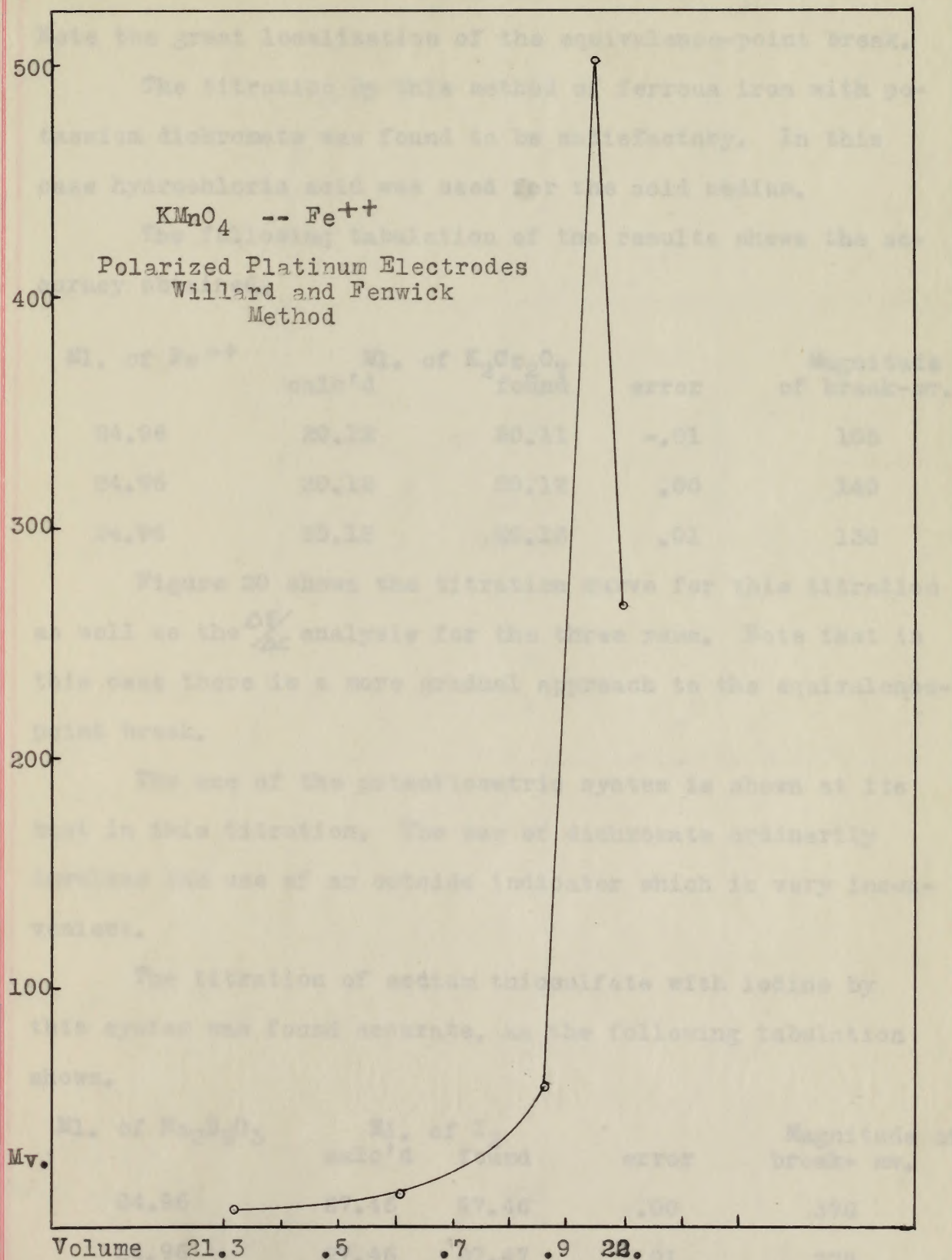
Cf. This thesis, p. 37-40.

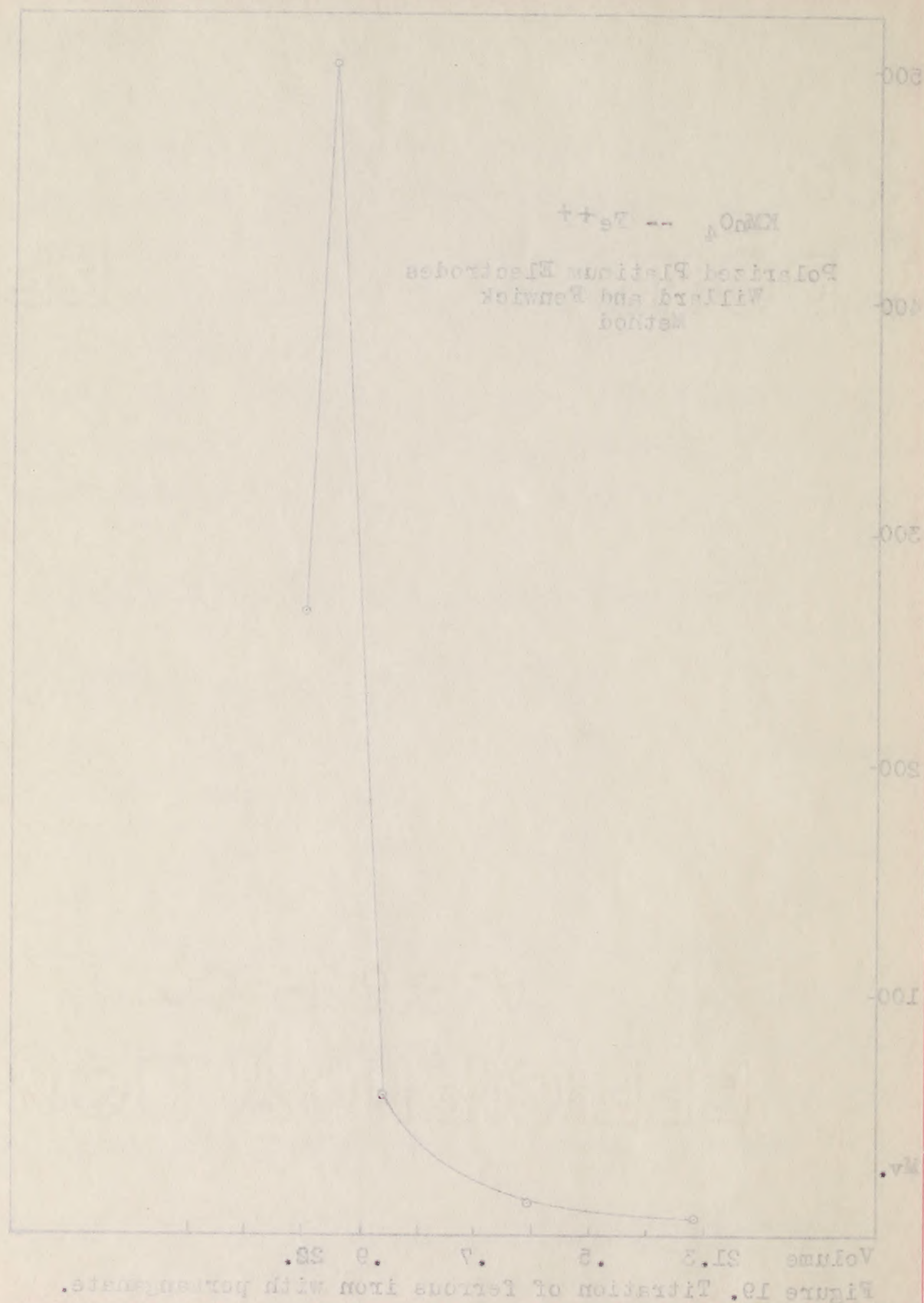
The apparatus was set up as is shown diagrammatically in Figure 10. The current was drawn from a potential of 5 volts through a resistance of 100,000 ohms. The polarizing current was, then, of the order of  $5 \times 10^{-6}$  amperes. This arrangement was found satisfactory for the reactions studied. The first reaction studied was the titration of ferrous ammonium sulfate with potassium permanganate. 25.98 milliliters of the ferrous solution was placed in the beaker with 250 milliliters of water and 10 milliliters of concentrated sulfuric acid. The following tabulation shows the results obtained.

Vol. of $KMnO_4$	Vol. of $Fe^{2+}$	Vol. of $Fe^{2+}$	Vol. of $Fe^{2+}$	Vol. of $Fe^{2+}$
Found	Calcd	Found	Calcd	Found
21.98	21.98	21.98	21.98	21.98
21.98	21.98	21.98	21.98	21.98
20.75	20.75	20.75	20.75	20.75
20.75	20.75	20.75	20.75	20.75

The results show this method to be accurate for this titration within the limits of experimental error. It is significant that one drop of permanganate over the potential equivalence-point gave the colorimetric end-point. Figure 19 shows a titration curve for this titration.









Note the great localization of the equivalence-point break.

The titration by this method of ferrous iron with potassium dichromate was found to be satisfactory. In this case hydrochloric acid was used for the acid medium.

The following tabulation of the results shows the accuracy obtained.

Ml. of $\text{Fe}^{++}$	Ml. of $\text{K}_2\text{Cr}_2\text{O}_7$		error	Magnitude of break-mv.
	calc'd	found		
24.96	20.12	20.11	-.01	105
24.96	20.12	20.12	.00	140
24.96	20.12	20.13	.01	130

Figure 20 shows the titration curve for this titration as well as the  $\frac{\Delta E}{\Delta C}$  analysis for the three runs. Note that in this case there is a more gradual approach to the equivalence-point break.

The use of the potentiometric system is shown at its best in this titration. The use of dichromate ordinarily involves the use of an outside indicator which is very inconvenient.

The titration of sodium thiosulfate with iodine by this system was found accurate, as the following tabulation shows.

Ml. of $\text{Na}_2\text{S}_2\text{O}_3$	Ml. of $\text{I}_2$		error	Magnitude of break- mv.
	calc'd	found		
24.96	27.46	27.46	.00	370
24.96	27.46	27.47	.01	270

Note the great localization of the equivalence-point break.  
The titration by this method of ferrous iron with potassium dichromate was found to be satisfactory. In this case hydrochloric acid was used for the acid medium.  
The following tabulation of the results shows the accuracy obtained.

Mg. of Fe <sup>++</sup>	Ml. of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> calc'd	Ml. of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> found	error	Magnitude of break-w.
24.96	20.12	20.11	-.01	102
24.96	20.12	20.12	.00	140
24.96	20.12	20.12	.01	130

Figure 20 shows the titration curve for this titration as well as the  $\frac{\Delta E}{\Delta V}$  analysis for the three runs. Note that in this case there is a more gradual approach to the equivalence-point break.

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Ml. of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Ml. of I <sub>2</sub> calc'd	Ml. of I <sub>2</sub> found	error	Magnitude of break-w.
24.96	27.46	27.46	.00	270
24.96	27.46	27.47	.01	270



## TITRATION CURVES

## POLARIZED PLATINUM ELECTRODES

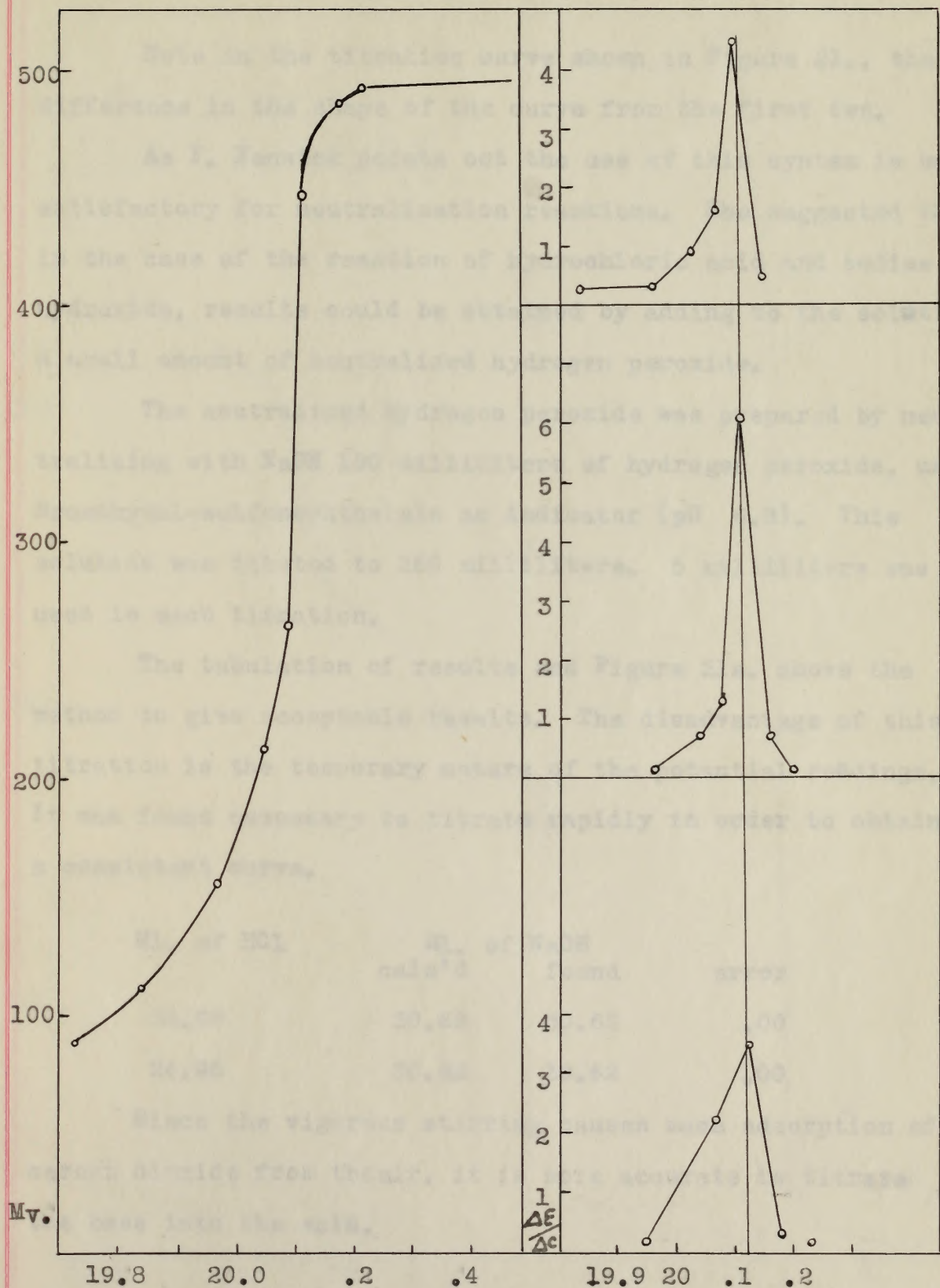


Figure 20. Ferrous iron with dichromate.

# TITRATION CURVES POLARIZED PLATINUM ELECTRODES

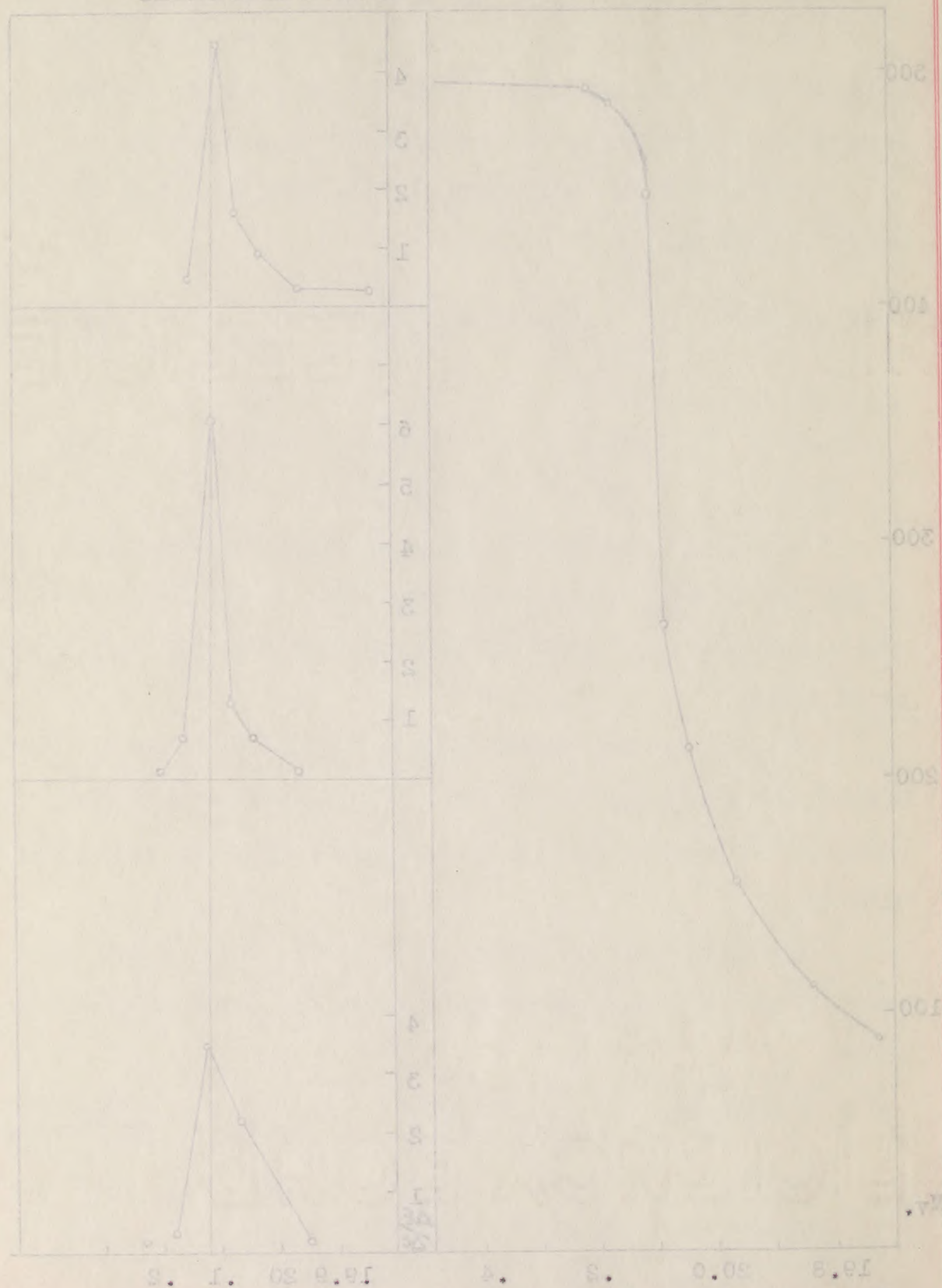


Figure 50. Ferrous iron with dichromate.



Note in the titration curve shown in Figure 21., the difference in the shape of the curve from the first two.

As F. Fenwick points out the use of this system is unsatisfactory for neutralization reactions. She suggested that in the case of the reaction of hydrochloric acid and sodium hydroxide, results could be obtained by adding to the solution a small amount of neutralized hydrogen peroxide.

The neutralized hydrogen peroxide was prepared by neutralizing with NaOH 100 milliliters of hydrogen peroxide, using Bromthymol-sulfonephthalein as indicator (pH 6.8). This solution was diluted to 250 milliliters. 5 milliliters was used in each titration.

The tabulation of results and Figure 21a. shows the method to give acceptable results. The disadvantage of this titration is the temporary nature of the potential readings. It was found necessary to titrate rapidly in order to obtain a consistant curve.

Ml. of HCl	Ml. of NaOH		error
	calc'd	found	
24.96	30.62	30.62	.00
24.96	30.62	30.62	.00

Since the vigorous stirring causes much adsorption of carbon dioxide from the air, it is more accurate to titrate the base into the acid.

Note in the titration curve shown in Figure 21, the

difference in the shape of the curve from the first two.

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The tabulation of results and Figure 21a, shows the

method to give acceptable results. The disadvantage of this

titration is the temporary nature of the potential readings.

It was found necessary to titrate rapidly in order to obtain

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	ml. of HCl	ml. of NaOH calcd	error
	24.98	30.62	.00
	24.98	30.62	.00

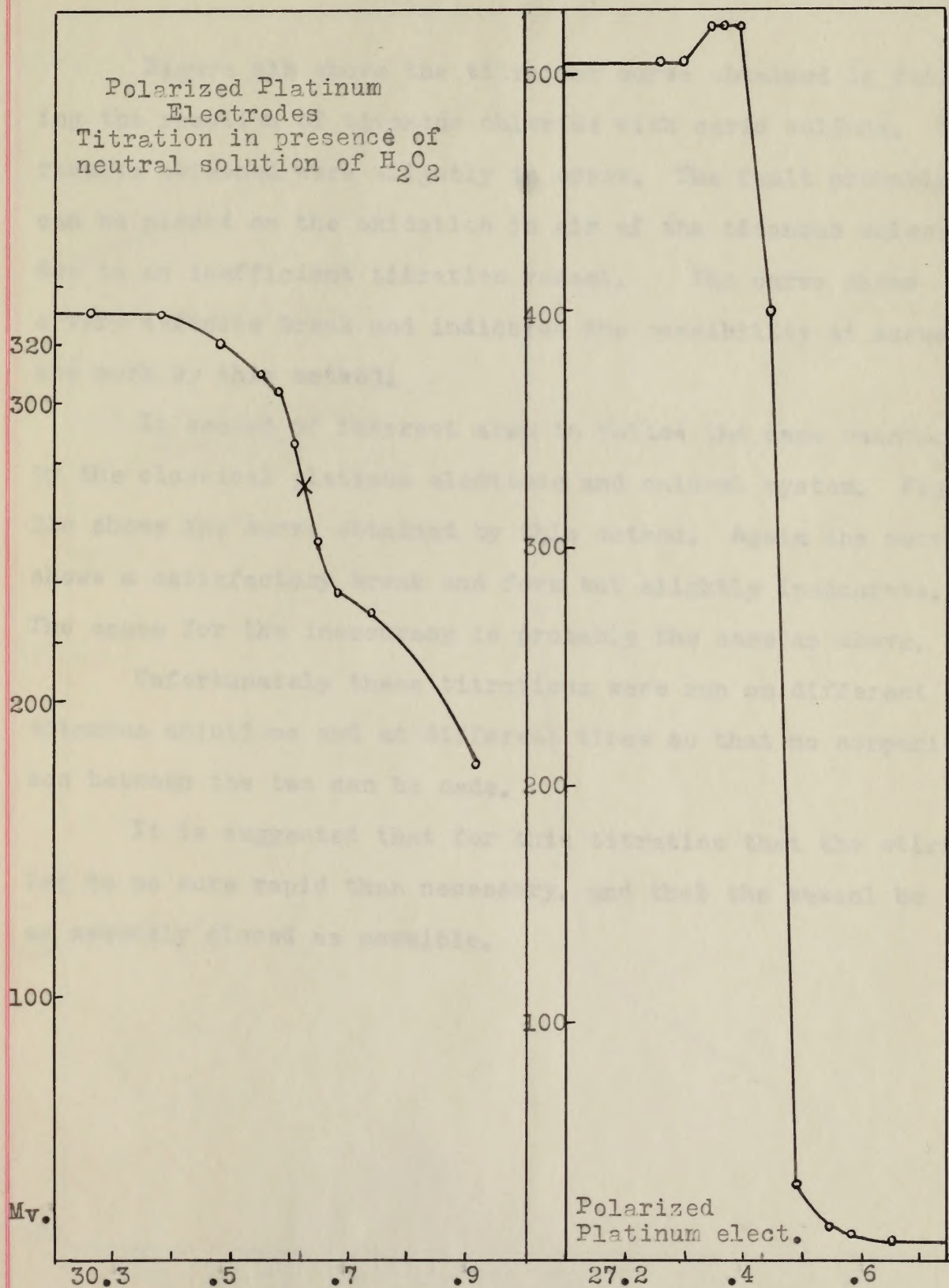
Since the vigorous stirring causes much absorption of

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the base into the acid.



## TITRATION CURVES



TITRATION CURVES

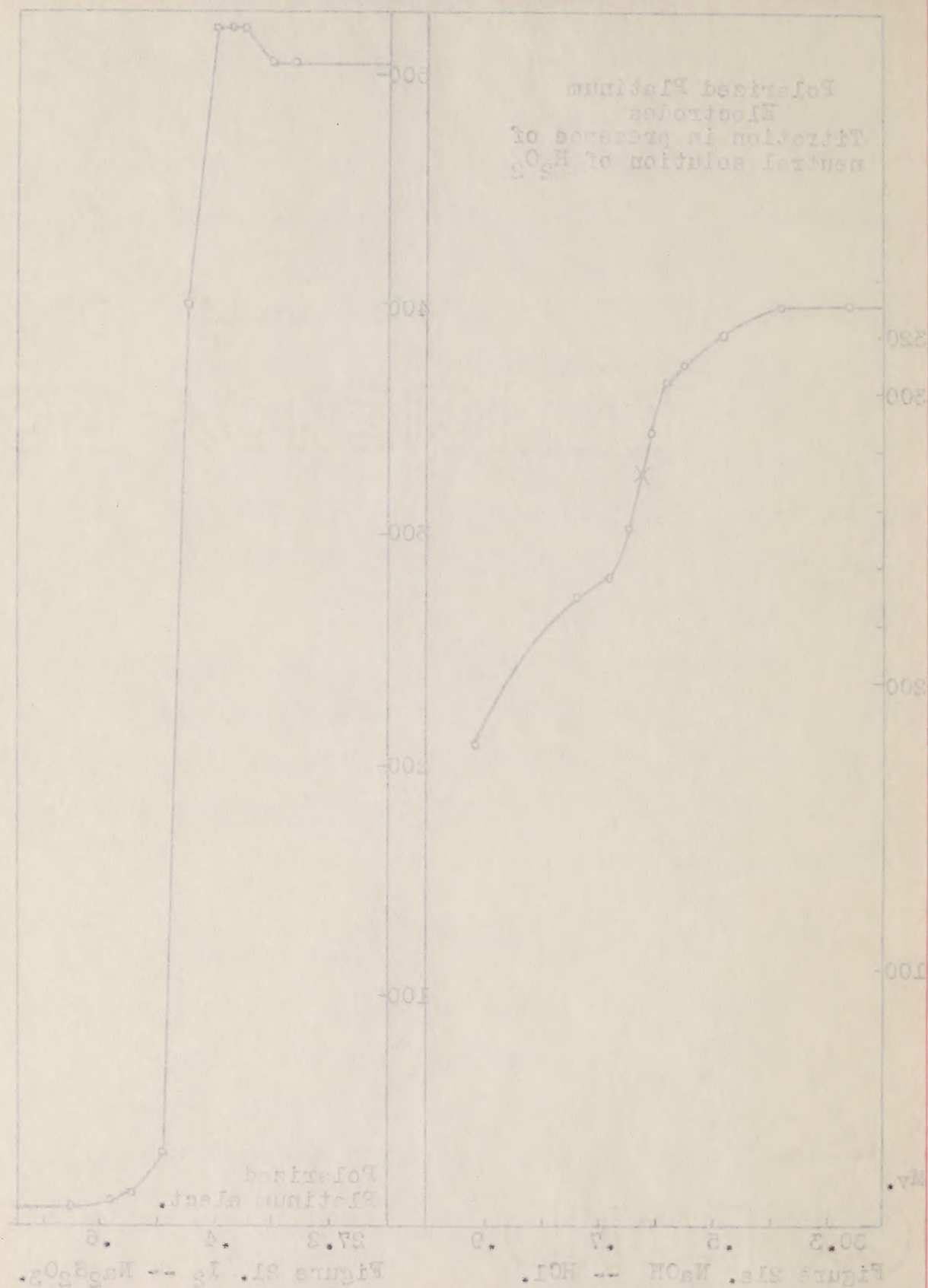




Figure 21b shows the titration curve obtained in following the reaction of titanous chloride with ceric sulfate. The results obtained were slightly in error. The fault probably can be placed on the oxidation in air of the titanous chloride due to an inefficient titration vessel. The curve shows a very definite break and indicates the possibility of accurate work by this method.

It seemed of interest also to follow the same reaction by the classical platinum electrode and calomel system. Figure 21c shows the curve obtained by this method. Again the curve shows a satisfactory break and form but slightly inaccurate. The cause for the inaccuracy is probably the same as above.

Unfortunately these titrations were run on different titanous solutions and at different times so that no comparison between the two can be made.

It is suggested that for this titration that the stirring be no more rapid than necessary, and that the vessel be as securely closed as possible.

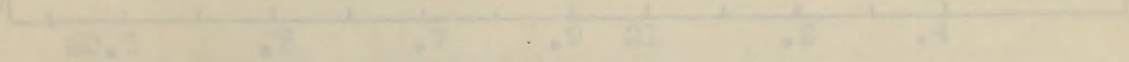


Figure 21b.

Figure 21b shows the titration curve obtained in following the reaction of titanium chloride with ceric sulfate. The results obtained were slightly in error. The fault probably can be placed on the oxidation in air of the titanium chloride due to an inefficient titration vessel. The curve shows a very definite break and indicates the possibility of securing work by this method.

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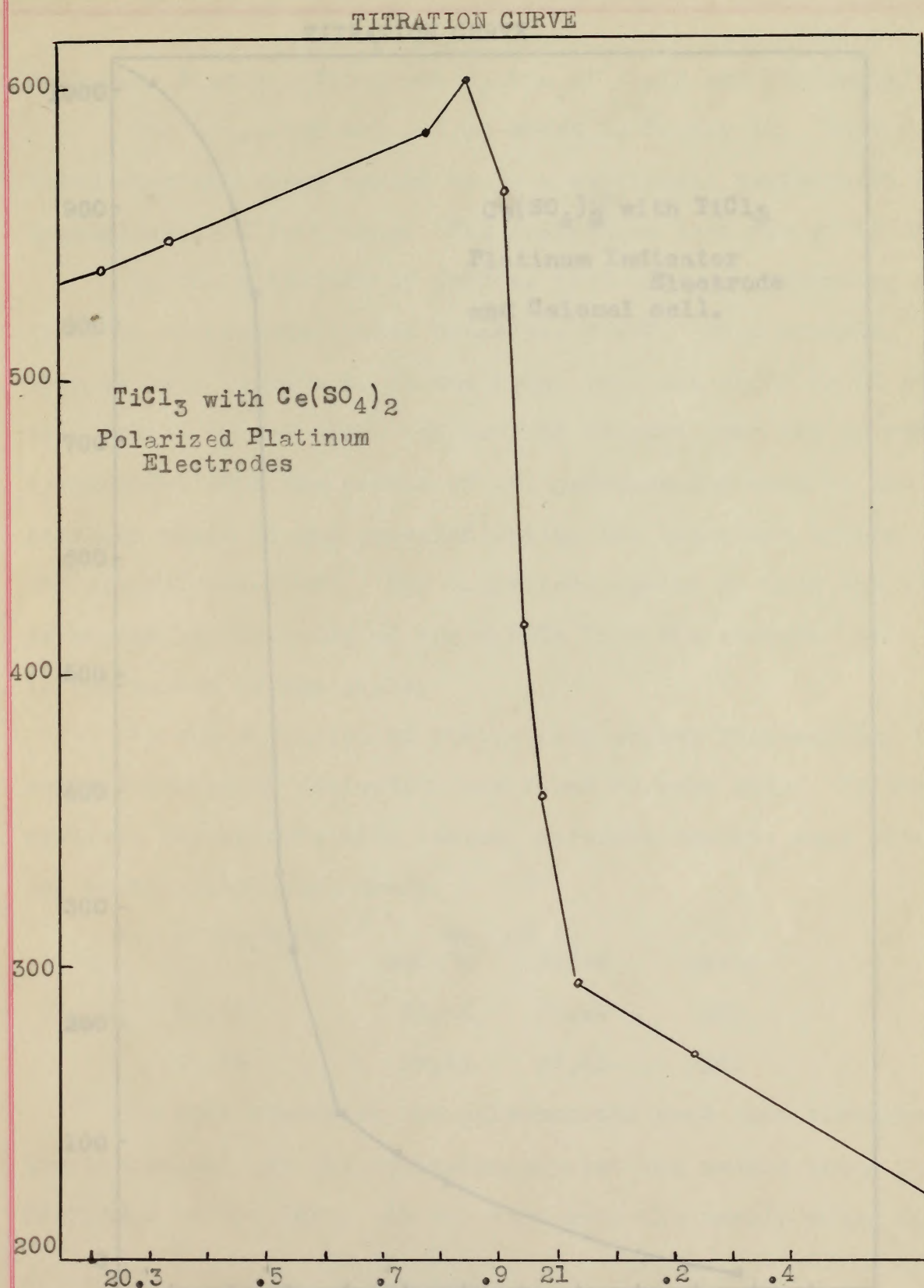
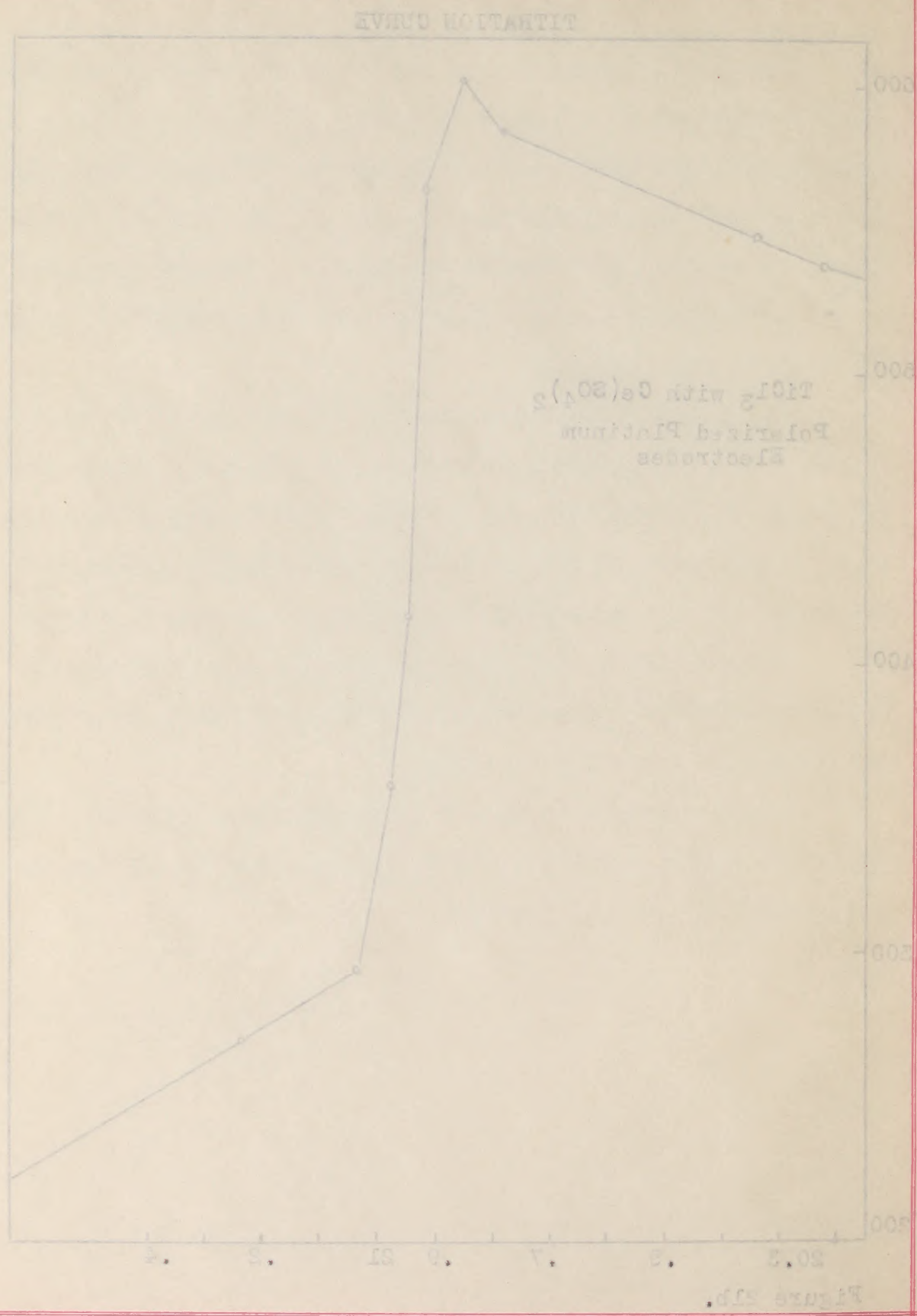


Figure 21b.





## TITRATION CURVE

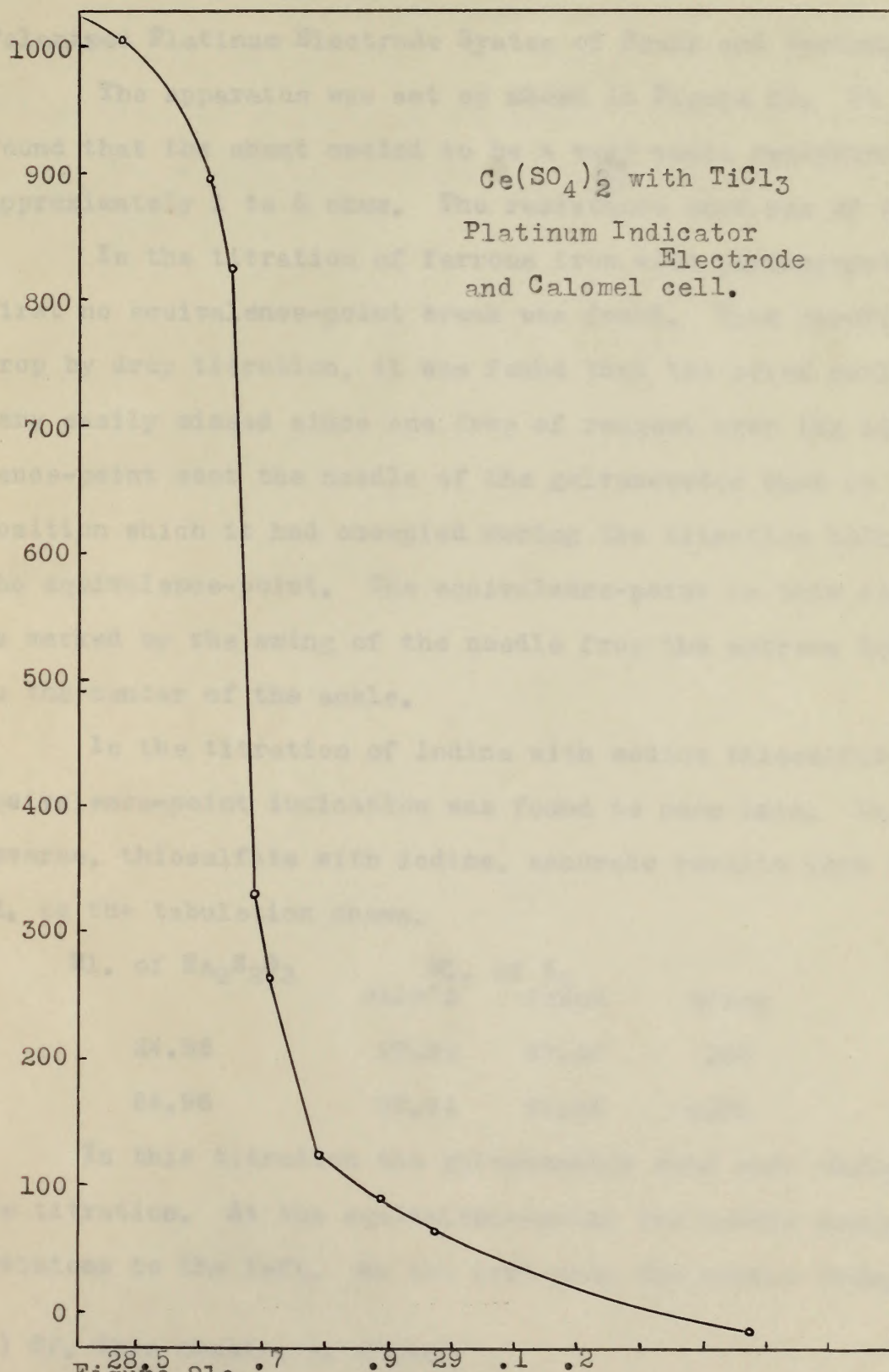
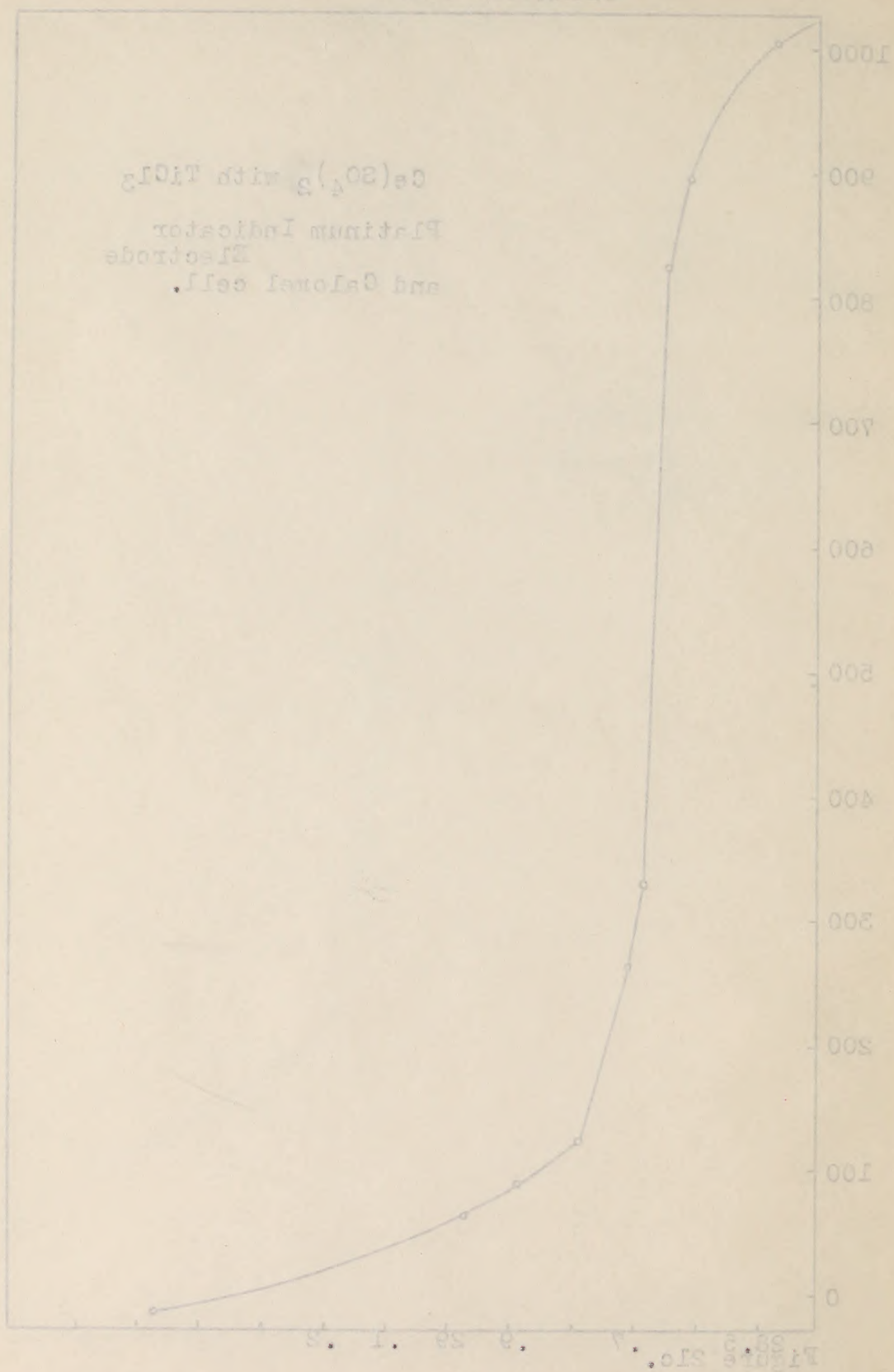


Figure 21c.

# TITRATION CURVE





# Polarized Platinum Electrode System of Foulk and Bawden.(1)

The apparatus was set up shown in Figure 13. It was found that the shunt needed to be a very small resistance, of approximately 1 to 5 ohms. The resistance used was of 48 ohms.

In the titration of ferrous iron with permanganate, at first no equivalence-point break was found. Upon careful, drop by drop titration, it was found that the point could be very easily missed since one drop of reagent over the equivalence-point sent the needle of the galvanometer back to the position which it had occupied during the titration before the equivalence-point. The equivalence-point in this reaction is marked by the swing of the needle from the extreme left to the center of the scale.

In the titration of iodine with sodium thiosulfate, the equivalence-point indication was found to come late. In the reverse, thiosulfate with iodine, accurate results were obtained, as the tabulation shows.

Ml. of $\text{Na}_2\text{S}_2\text{O}_3$	Ml. of $\text{I}_2$		error
	calc'd	found	
24.96	27.44	27.44	.00
24.96	27.44	27.43	-.01

In this titration the galvanometer read zero throughout the titration. At the equivalence-point the needle swung four divisions to the left. At the next drop the needle swung to

(1) Cf. This thesis, p. 47,48.

Polarized Platinum Electrode System of Foulk and Bowden, (1)

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(1) Cf. This thesis, p. 47, 48.



the extreme left and the solution turned a light yellow. It is interesting to note that when a starch solution is added to the titrated solution at the potentiometric equivalence-point, the reading is destroyed by the swing of the needle back towards zero.

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### Polarization Phenomena.

In the platinum electrode systems of both Willard and Fenwick and that of Foulk and Bawden the equivalence-point phenomena is explained on the basis of polarization effects.

Experiments were made to verify their explanations and to study these effects.

A circuit was devised similar to the titration system of Foulk and Bawden differing in the placing of the electrodes. The electrodes, of bright platinum, were placed in separate beakers. The circuit was completed with a salt bridge. By this system the effect of the various solutions could be determined on each electrode.

The iodine - thiosulfate system was first studied. The beakers were filled with dilute sulfuric acid as well as the salt bridge. A millivoltmeter was connected through a tapping key across the electrodes.

When the potential of a dry cell through about 45 ohms was placed across the electrodes the galvanometer read zero. The potential read on the voltmeter was 35.3 mv. When the polarizing current was removed, the galvanometer swung away from zero showing that the electrodes had been polarized.

The electrodes were again polarized and the effect of the reacting solutions on both electrodes were studied.

It is to be remembered that Foulk and Bawden stated that throughout this titration the anode was depolarized and that at the equivalence-point both electrodes were depolarized.

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key across the electrodes.

When the potential of a dry cell through about 40 ohms  
was placed across the electrodes the galvanometer read zero.  
The potential read on the voltmeter was 36.5 mv. When the  
polarizing current was removed, the galvanometer swung away from  
zero showing that the electrodes had been polarized.

The electrodes were again polarized and the effect of  
the reacting solutions on both electrodes were studied.  
It is to be remembered that Foulk and Bawden stated that  
throughout this titration the anode was depolarized and that  
at the equivalence-point both electrodes were depolarized.



The following tabulation shows the results of this experiment.

Anode beaker	Cathode beaker	Galvanometer reading	Millivolt-meter reading
dil. $\text{H}_2\text{SO}_4$	dil. $\text{H}_2\text{SO}_4$	0	35.3
I added	"	10	34
I	I	extreme	34
I	excess Thiosulfate	0	35.3
excess Thiosulfate	excess I	12	34.2
"	excess Thiosulfate	0	35.3

The results show agreement with the theory and work of Foulk and Bawden. It is seen that the anode is depolarized by either the thiosulfate or potassium iodide and the cathode by an excess of iodine.

A similar experiment was carried out with the reaction of ferrous iron and permanganate. Solutions of ferrous iron, ferric iron and permanganate were used.

The following tabulation shows the results.

Anode beaker	Cathode beaker	Galvanometer reading	Millivolt-meter reading
dil. $\text{H}_2\text{SO}_4$	dil. $\text{H}_2\text{SO}_4$	0	35.3
Ferrous sol'n	"	4	34.8
"	Ferric iron	5	34.8
$\text{KMnO}_4$ to faint pink	$\text{KMnO}_4$ to faint pink	0	35.3

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periment.

Anode beaker	Cathode beaker	Galvanometer reading	Millivolt-meter reading
dil. $H_2SO_4$	dil. $H_2SO_4$	0	35.2
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Anode beaker	Cathode beaker	Galvanometer reading	Millivolt-meter reading
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Ferrous solution	"	4	34.8
"	Ferric iron	5	34.8
$KMnO_4$ to faint pink	$KMnO_4$ to faint pink	0	35.2



Anode beaker	Cathode beaker	Galvanometer reading	Millivolt-meter reading
Ferrous iron	$\text{KMnO}_4$	10	34.4
Excess $\text{KMnO}_4$	Excess $\text{KMnO}_4$	0	34.5

This experiment shows that both the ferrous and ferric solutions have a depolarizing effect on the anode and cathode respectively but that in the presence of permanganate the depolarizing effect of the ferric iron is not felt. This agrees with the statements concerning this reaction by Willard and Fenwick.

In this titration the ferrous sulfate was titrated with iodine and found to give accurate results. The electrodes were placed as the diagram suggests. This method of placing electrodes was found to give a good indication of the approach of the equivalence-point.

#### Tabulation of results

Ml. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Ml. of $\text{I}_2$		error
	calc'd	found	
24.95	27.44	27.43	-.01
24.95	27.44	27.46	.01

It was of interest to follow completely the course of the galvanometer reading during the titration. The reagent solution was allowed to flow into the beaker drop by drop and the galvanometer carefully watched. The galvanometer reading did not vary from zero until 25 ml. had been titrated in, then kicked temporarily to the left. At 26 ml. the needle started

(1) Cf. This thesis, 53.

Anode basket	Cathode basket	Galvanometer	Millivolt-
		reading	meter reading
Ferrous iron	$KMnO_4$	10	34.4
Excess $KMnO_4$	Excess $KMnO_4$	0	34.5

This experiment shows that both the ferrous and ferric solutions have a depolarizing effect on the anode and cathode respectively but that in the presence of permanganate the depolarizing effect of the ferric iron is not felt. This agrees with the statements concerning this reaction by Willard and Fenwick.



# The Continuous-Reading System of Kassner, Hunge and Chatfield. (1)

The apparatus for this system is shown diagrammatically in Figure 16.

In the titration of ferrous iron with permanganate, no equivalence-point break was found. It is suggested that this is probably due to the fact that the break is of a very abrupt nature and may have been missed, as was found true in the case of the same titration in the Foulk and Bawden system.

Sodium thiosulfate was titrated with iodine and found to give accurate results. The electrodes were placed as the diagram suggests. This method of placing electrodes was found to give a good indication of the approach of the equivalence-point.

## Tabulation of results:

Ml. of $\text{Na}_2\text{S}_2\text{O}_3$	Ml. of $\text{I}_2$		error
	calc'd	found	
24.96	27.44	27.43	-.01
24.96	27.44	27.46	.02

It seemed of interest to follow completely the course of the galvanometer reading during the titration. The reagent solution was allowed to flow into the beaker drop by drop and the galvanometer carefully watched. The galvanometer reading did not vary from zero until 23 ml. had been titrated in, then kicked temporarily to the left. At 26 ml. the needle started

(1) Cf. This thesis, 53.

The apparatus for this system is shown diagrammatically

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Sodium thiosulfate was titrated with iodine and found to give accurate results. The electrodes were placed as the diagram suggests. This method of placing electrodes was found to give a good indication of the approach of the equivalence-point.

Tabulation of results:

error	ml. of $I_2$ found	ml. of $Na_2S_2O_3$ calc'd	ml. of $Na_2S_2O_3$
-0.01	27.43	27.44	24.96
0.02	27.46	27.44	24.96

It seemed of interest to follow completely the course of

the galvanometer reading during the titration. The reagent solution was allowed to flow into the beaker drop by drop and the galvanometer carefully watched. The galvanometer reading did not vary from zero until 23 ml. had been titrated in, then kicked temporarily to the left. At 26 ml. the needle started



to swing to the right, increasing in that direction as the titration proceeded. At 26.98 ml. there was a kick to the left. At 27.40 the needle started toward zero. On the next drop the needle swung completely to the left of the scale. The indication of the approaching equivalence-point was, therefore, effecient.

In this titration too, the addition of a starch solution was found to destroy the equivalence-point indication.

Potassium dichromate was titrated with ferrous iron. In this titration the position of the electrodes was reversed. The galvanometer readings were found to be similar to those found in the preceding titration.

The tabulation of the results shows the titration to be accurate.

Ml. of $K_2Cr_2O_7$	Ml. of $Fe^{++}$		
	calc'd.	found	error
24.96	33.54	33.53	-.01
24.96	33.54	33.55	.01

In both of these titrations a shunt of 20,000 ohms was used and a grid potential of 1.5 volts.

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The tabulation of the results shows the titration to be accurate.

ml. of $K_2Cr_2O_7$	ml. of $Fe^{++}$	error
24.96	33.53	-0.01
24.96	33.53	0.01

In both of these titrations a current of 20,000 ohms was used and a grid potential of 1.5 volts.



### Burette Electrode. (1)

This burette electrode seemed to offer a simple system using the unattackable electrode system of platinum. A burette was constructed as shown in Figure 7. To prevent the sealed-in platinum wire from breaking at the point of seal on the outside, a metal tip was used. This metal tip was obtained from an ordinary radio power tube. It was fastened to the burette with Dekotinski cement and the platinum wire soldered to the metal. This was found to be an efficient method of safeguarding the platinum wire and made a good contact.

Titration of ferrous iron with permanganate, this system was found to be successful as the tabulation shows.

Ml. of $\text{Fe}^{++}$	Ml. of $\text{KMnO}_4$ calc'd	Ml. of $\text{KMnO}_4$ found	error	Magnitude of break-mv.
24.96	20.63	20.63	.00	449
24.96	20.63	20.64	.01	495

Figure 22 shows the curve for this titration.

The titration of sodium hydroxide and hydrochloric acid was not satisfactory. A break was obtained but not of sufficient sharpness.

The use of the tip of the burette as a salt bridge causes no error by diffusion. An incidental advantage of the tip extending into the solution is that amounts of the reagent smaller than one drop may be added with great ease.

(1) Cf. This thesis, p. 24,25.

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M. of $Pb^{++}$	calc'd	M. of $KMnO_4$ found	error	Magnitude of break-w.
24.96	20.63	20.63	.00	449
24.96	20.63	20.64	.01	492

Figure 22 shows the curve for this titration. The titration of sodium hydroxide and hydrochloric acid was not satisfactory. A break was obtained but not of sufficient sharpness.

The use of the tip of the burette as a salt bridge caused no error by diffusion. An incidental advantage of the tip extending into the solution is that amounts of the reagent smaller than one drop may be added with great ease.



## TITRATION CURVES

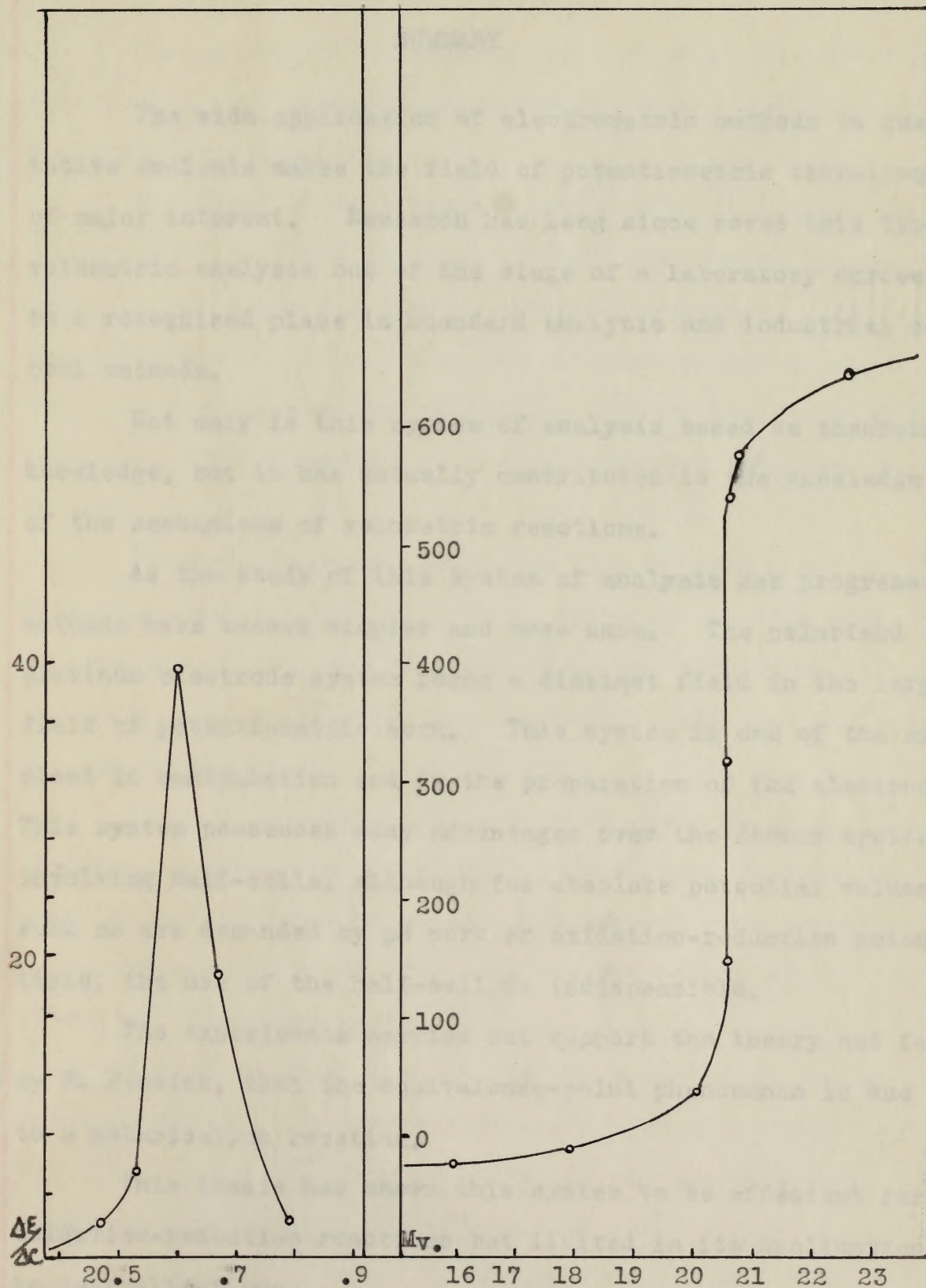


Figure 22. Fe --KMnO<sub>4</sub>. Titration with burette electrode.

# TITRATION CURVES

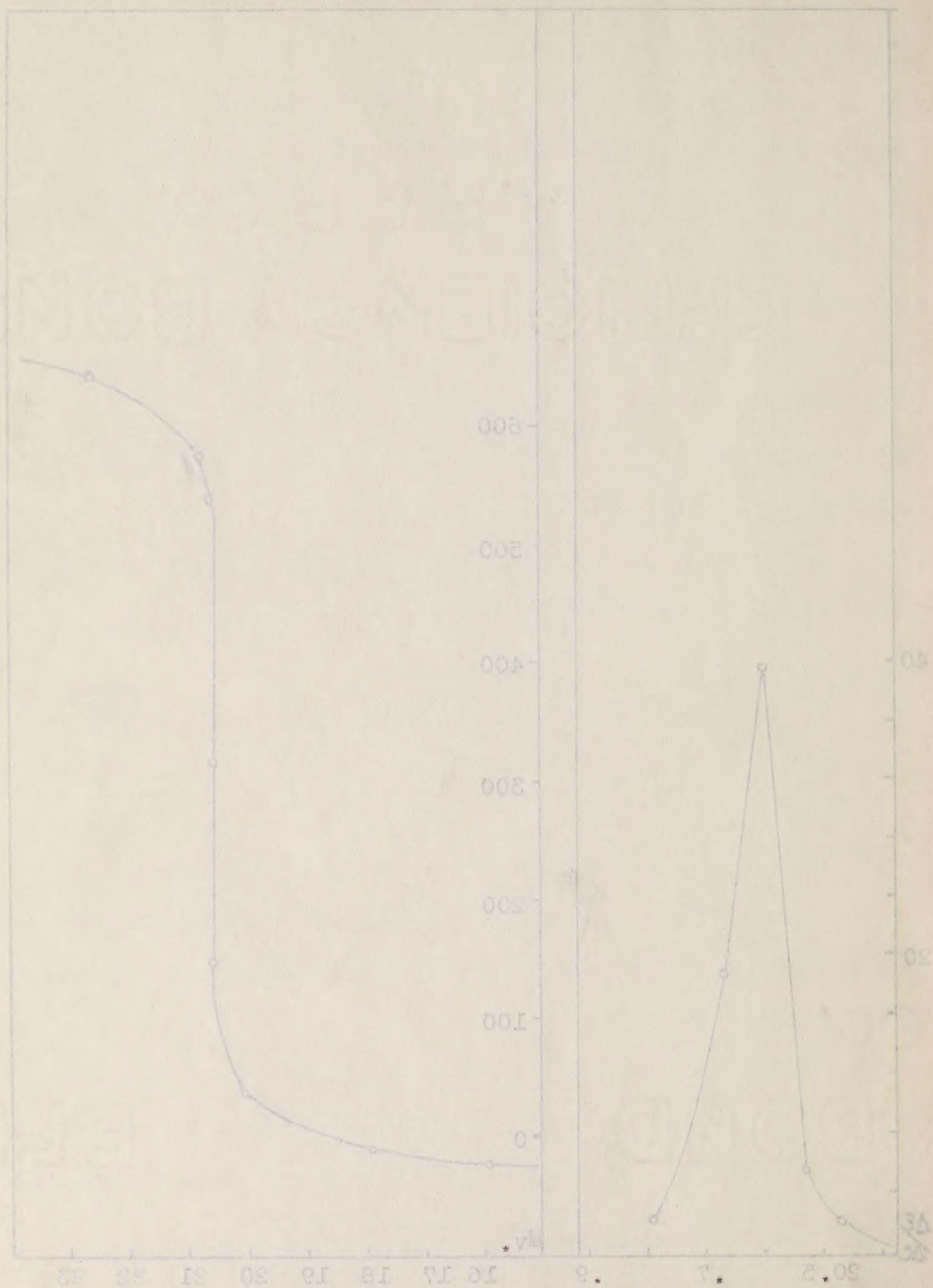


Figure 28. Fe--K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Titration with butyrate electrode.



## SUMMARY

The wide application of electrometric methods in quantitative analysis makes the field of potentiometric titrations of major interest. Research has long since moved this type of volumetric analysis out of the stage of a laboratory curiosity to a recognized place in standard analytic and industrial control methods.

Not only is this system of analysis based on theoretic knowledge, but it has actually contributed to the knowledge of the mechanisms of volumetric reactions.

As the study of this system of analysis has progressed, methods have become simpler and more sure. The polarized platinum electrode system forms a distinct field in the larger field of potentiometric work. This system is one of the simplest in manipulation and in the preparation of the electrodes. This system possesses many advantages over the former systems involving half-cells, although for absolute potential values, such as are demanded by pH work or oxidation-reduction potentials, the use of the half-cell is indispensable.

The experiments carried out support the theory set forth by F. Fenwick, that the equivalence-point phenomenon is due to a polarization reaction.

This thesis has shown this system to be efficient for oxidation-reduction reactions but limited in its application to neutralizations.

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The scientific literature contains many articles on other bimetallic systems, many of which were found accurate for neutralization reactions.

A simpler system, based on principles similar to the system of Willard and Fenwick, of Foulk and Bawden has been found satisfactory for certain types of reactions. While it has the advantage of being of the continuous-reading type, it has also the disadvantage of lacking an equivalence-point warning. This disadvantage may be corrected by proper modification.

Kassner, Hunge and Chatfield have devised a system based also upon these principles. It is efficient for the same type of reaction. It should be noted that this circuit is limited in use to this particular type of reaction and does not have a broad applicability.

The continuous-reading apparatus of Goode or similar devices, in which the plate current is a known function of the grid potential, seems to be the best type of continuous-reading apparatus for all types of reactions. It can be applied to nearly all electrode systems.

For electrodes, such as the glass electrode, which are characterized by a high resistance a system such as that of Partridge is recommended, in which the circuit acts as a very sensitive galvanometer for the potentiometer circuit.

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